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COLLABORATIVE STUDY OF REFERENCE METHOD FOR MEASUREMENT OF PHOTOCHEMICAL OXIDANTS IN THE ATMOSPHERE (OZONE-ETHYLENE CHEMILUMINESCENT METHOD)

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Southwest Research Institute

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16. ABSTRACT

This report contains information on collaborative tests to determine the precision and bias of the reference method for measurement of photochemical oxidants as published by the Environmental Protection Agency in the *Federal Register*, April 30, 1971.

In the first phase test, ten collaborators were assembled at a common site to measure (from a common source) ambient and ozone supplemented concentrations over a range from 0 to 0.510 ppm (0-1000μg/m³). The data were analyzed to derive an estimate for the precision of the method. Estimates of the standard deviations of the process for total (S_T), between-laboratory (S_L) and within-laboratory (S_{WL}) were derived, as well as for the lower detectable limit (*LDL*). The results were:

$$S_T = 0.0033 + 0.0412\,x \qquad 0 < x \leq 0.153$$
$$S_T = -0.0017 + 0.068\,x \qquad 0.153 < x \leq 0.510$$
$$S_L = 0.0008 + 0.0355\,x \qquad 0 < x \leq 0.513$$
$$S_L = -0.0051 + 0.0690\,x \qquad 0.153 < x \leq 0.510$$
$$S_{WL} = 0.0033 + 0.0255\,x \qquad 0 < x \leq 0.510$$

where x is the concentration level in ppm.

$$LDL = 0.0065 \text{ ppm.}$$

The second phase consisted of a collaborative test involving eleven laboratories to determine the accuracy (bias) of the method. Ozone generating systems (synthetic atmosphere) which had been calibrated by the National Bureau of Standards were supplied to each collaborator. Five concentration levels (known to the test designer) were measured at each laboratory. Ten laboratories completed the test, and useful data were supplied by nine laboratories. The results are as follows:

Over the range of 0 to 0.500 parts per million, a systematic negative bias exists in the method. The upper limit of the 95% confidence interval on the observed average ranged from 9 to 29 percent below the true values, and the lower limit varied from 20 to 45 percent below the true values.

The mean percentage difference between the average observed value and the true value at the five concentration levels ranged from 15.9 to 37.3 percent.

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ABSTRACT

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The assistance and cooperation of the participating laboratories is acknowledged with sincere appreciation for the voluntary efforts of the staff members who represented each organization. The names and affiliations of the representatives completing the test for the first phase were as follows:

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I. INTRODUCTION

Ozone and related chemical contaminants in the atmosphere have been measured for many years to obtain an estimate of the nature and extent of a unique type of air pollution commonly termed "photochemical smog". This unique type of air pollution was first identified in the Los Angeles area during the early 1950's, and has since become more prevalent in many urban areas throughout the country. It is formed when organic matter (largely hydrocarbons) reacts with nitrogen dioxide in the presence of sunlight to produce a complex mixture of reaction products which in turn are responsible for eye irritation, a unique type of vegetation damage, the formation of haze which restricts visibility, and other manifestations of photochemical smog. Ozone and other highly oxidizing substances are also produced in this reaction mechanism.

For many years, a measurement designated by the catchall term "oxidant" was used as a measure of photochemical smog. This measurement was obtained by measuring the iodine released from potassium iodide solution when the air sample was bubbled through, and represented the net total of all of the oxidizing substances minus any reducing substances (such as sulfur dioxide) which might also be present. It was generally recognized that the primary component of the oxidant was ozone although oxides of nitrogen, peroxides, and other constituents also contributed to the total oxidant measurement.

In setting ambient air quality standards under the mandates of the 1970 Amendments to the Clean Air Act, the Environmental Protection Agency selected a chemiluminescent method of measurement rather than the potassium iodide method since the former is specific for ozone. In this method, the air stream is mixed with a stream of ethylene, and any ozone present reacts with the ethylene by a chemiluminescent reaction mechanism. The light produced during this reaction is then measured by a photo-electric device in order to determine the amount of ozone present in the original air stream. The instrument is calibrated by synthetic atmospheres using an ozone generator which in turn has been calibrated by the potassium iodide method. Commercial instruments are available which provide a continuous recording of the ozone levels being measured.

In order to obtain reliable data in measuring ozone and other atmospheric contaminants to determine compliance with the ambient air quality standards, the Environmental Protection Agency (EPA) Methods Standardization and Performance Evaluation Branch (MSPEB) has been working for some time to develop standard methods which could be used by all persons making air quality measurements. Following the development of a tentative standard method, the final step in the standardization process is a collaborative test, or interlaboratory comparison, of the proposed standard method. This procedure, also called "round-robin testing", has been used to evaluate many different methods of measurement in such diverse fields as water chemistry, metallurgy, paint and surface coatings, food and related products, and many others. A test of this nature by a representative group of laboratories is the only way that the statistical limits of error inherent in any method can be determined with sufficient confidence. With this goal in mind, the two collaborative tests described in this report were conducted by the MSPEB and Southwest Research Institute.

There were two primary objectives of the collaborative tests. The first objective was to derive an estimate of the precision of the Standard Method, and the second was to derive an estimate of the bias of the Standard Method. Throughout the body of this report, the first test (to determine the precision of the method) will be referred to as Phase I, and the second test (to determine the bias of the method) will be referred to as Phase II.

In the Phase I collaborative test, a group of participating laboratories gathered at a single location in order to run simultaneous tests on a "real life" atmosphere typical of photochemical smog. The results of this collaborative test were then analyzed statistically to determine the precision of the proposed method.

In the Phase II collaborative test, each of the ten participants worked in his own laboratory and a standard ozone source for five concentration levels was provided to each of the test collaborators. Each collaborator prepared an I_2 versus absorbance graph for various standard iodine solutions and calibration curves for the monitoring

instruments, according to the method (see Appendix A). The collaborators then used the method to analyze the ozone levels generated by the standard.

This report describes the design of the experiments, the statistical analysis, and the results of the two collaborative tests.

II. COLLABORATIVE TESTING OF THE METHOD

An important step in the standardization of any method of measurement is collaborative testing to determine, on a statistical basis, the limits of error which can be expected when the method is used by a typical group of investigators. The collaborative, or inter-laboratory, test of a method is an indispensable part[1] of the development and standardization of an analytical procedure to insure that 1) the procedure is clear and complete and that, 2) the procedure does give results with precision and accuracy in accord with those claimed for the method. Among other organizations, the Association of Official Analytical Chemists (AOAC) and the American Society for Testing and Materials (ASTM) have been active in the field of collaborative testing and have published guidelines of the proper procedure for conducting collaborative tests and evaluating the data obtained.[2-5] Publications of both organizations were used extensively in planning and conducting the collaborative tests of this method to measure ozone.

The first phase of the collaborative test involved the assembly of ten collaborators at a single site to measure ozone concentrations in ambient air to allow determination of the precision of the method. This phase of the test was conducted in Pasadena, California, during the month of September, 1972. This report describes the results of that test. The second phase involved the measurement of synthetic ozone atmospheres by the collaborators working in their own laboratories to determine the accuracy of the method.

A. Selection of Location

1. Phase I (Precision)

Since a synthetic mixture duplicating all of the characteristics of photochemical smog is difficult to prepare and standardize in the laboratory, it was decided to conduct an "on site" test in which participants would sample an ambient atmosphere under photochemical smog conditions. Since Los Angeles has been the prime example of an urban photochemical smog problem for many years, and since this type of air pollution occurs more frequently in Los Angeles than in other cities, it was decided to conduct this test in the Los Angeles area.

In order to select a suitable location, long-term monitoring data obtained from the Los Angeles County Air Pollution Control District were examined in order to determine the frequency and severity of photochemical smog in different portions of this urban area. This agency has maintained a comprehensive monitoring program for a number of years to measure oxidant and other contaminants throughout Los Angeles County to provide information for a vigorous ongoing program of air pollution control.

Of the various stations in this monitoring network, it was found that two stations showed the highest consistent levels of oxidant, one in Pasadena and one in Azuza. Both of these cities are located north and northeast of the city of Los Angeles itself, close to the mountain range which forms the northern boundary of the air basin and thus influences the degree of air stagnation which frequently occurs. Because of the meteorology and topography of the area, it is not surprising that the Pasadena-Azuza area should consistently show the highest levels of oxidant throughout the entire area.

So far as time was concerned, it has long been known that the most severe smog season occurs in the summer and early fall. Therefore, it was no surprise to find that the monitoring records indicated the most frequent occurrence of photochemical smog and the highest oxidant levels in the months of August, September, and October.

With this background information as a guide, suitable time and place for the collaborative test was next investigated. Through the cooperation of the California Institute of Technology in Pasadena, arrangements were made to conduct the test at an engineering laboratory building on the campus during the period between the summer and fall semesters. Fortunately, both the location and the time of year were favorable with respect to the probability of occurrence of high oxidant levels.

2. Phase II (Bias)

The locations of the Phase II test were fixed by the location of the individual collaborators, and represented various geographic areas of the continental United States.

B. Selection of Collaborators

1. Phase I (Precision)

If a collaborative test is to achieve the desired objective, it is desirable that the participants in the test be representative of the large group that will ultimately use the method being tested. Since air pollution measurements are made by many different groups, it is desirable to include in the group of collaborators a representative mix of those people making the pollution measurements. Final selection of participants included two from federal laboratories, five from state and local air pollution control agencies, two from industry, and one from a research institution. A list of the participants completing the test is included in the Acknowledgment.

Even more important than the type of laboratory is the degree of skill and experience of the persons who participated. Each laboratory was asked to assign a person to this test who had previous experience with the chemiluminescent method for measuring ozone and was competent in carrying out measurements by this method. This places emphasis upon the capabilities of the method rather than the performance of the laboratories.

2. Phase II (Bias)

The rationale for selection of collaborators in Phase II was the same as for Phase I. For Phase II, eleven collaborators were selected, nine of whom had participated in the first phase. Of the eleven, two were from governmental agencies, six from local and state air pollution control agencies, two from industry, and one from a research institution. Ten collaborators completed the test. A list of the participants is included in the Acknowledgment.

C. Providing Test Samples

1. Phase I (Precision)

In the study, test samples were provided by two different methods, each of which is described in detail below.

a. Ambient Atmospheres

A schematic diagram of the sampling system is shown in Figure 1. In the ambient air sampling mode, Valve A is closed and Valve B is opened. (Valve B is a safety pressure release for the ozone generation system). In this configuration, ambient air is brought in through a 3/4-in. diameter Teflon tube approximately 8-ft long extending through the window of the test room. The sampling line terminates on the outside of the building with a 90° bend pointed downward for protection in case of rain. All lines in contact with ozone are either of glass or Teflon. No pumps are required, and the ozone instruments draw air through Teflon intake lines from the common glass manifold. The glass manifold was designed, constructed, and tested in the Houston Laboratory prior to its installation in the test area. It was also rechecked after installation. A manometer on one of the ports of the manifold can be observed periodically to check pressure drops which were always less than 1/2-in. of water vacuum. The flow rate through the system in this manner is approximately 1 liter per minute per instrument for a total of about 10 liters per minute. A trap was installed in front of the manifold to collect condensate or particulate matter and keep it from entering the sample manifold. This trap proved to be unnecessary for this purpose since neither condensate nor particulate matter ever accumulated. A thermometer was also incorporated in the sampling manifold to periodically monitor temperature of ambient air. The ozone instrument discharge lines were connected to a glass manifold similar to the intake manifold to prevent ethylene buildup in the test area. This discharge manifold was connected by Tygon tubing approximately 30-ft long ex-

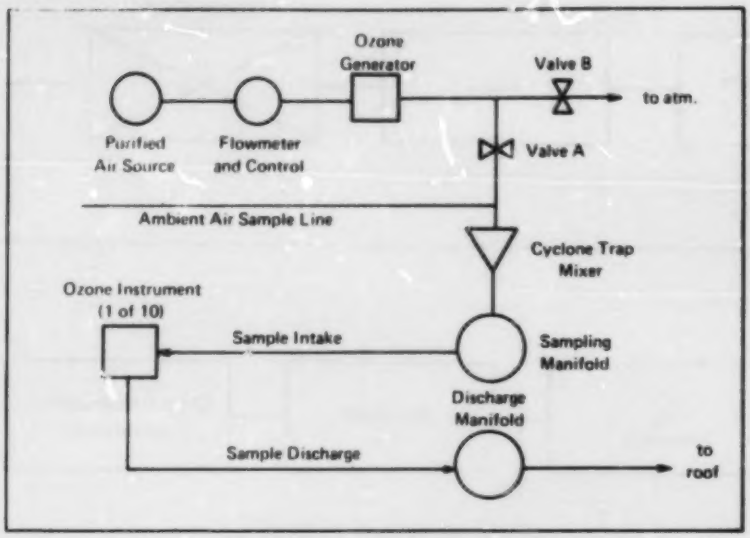

FIGURE 1. SCHEMATIC DIAGRAM OF SAMPLING SYSTEM
(Phase I)

tending to the roof of the three-story building. The pressure in the discharge manifold was consistently under 1 inch of water. This system operated satisfactorily in every respect.

b. Atmospheres Containing Supplemental Ozone

Ambient atmospheres containing supplemental ozone were provided by the same system shown in Figure 1 with Valve A open and Valve B closed. Operation of the ozone generation system was required in this mode. Purified air was obtained from compressed air cylinders (dry grade, with dew point -75°F maximum). Cartridge type purifiers were used to remove oil, water, and particles larger than 12 microns. Dew points of -100°F were thus achievable. The flow of purified air was controlled by a needle valve and a mass flowmeter on each of three ozone generators. Three ozone generators (NBS Technical Note 585) were required to provide the quantity needed for synthetic atmosphere generation. The purified air flow rate was adjusted to approximately 1 liter per minute. In this manner, approximately 9 liters per minute of ambient air were mixed with 1 liter per minute of a synthetic ozone-air mixture to provide an ambient air test sample containing supplemental ozone. The cyclone trap in front of the manifold served as a mixing chamber and insured thorough mixing of ambient air and synthetic ozone mixtures prior to entering the sampling manifold. Adding supplemental ozone to ambient atmospheres was never incorporated during the daytime hours in order that normal daily variations could be observed. As is obvious, the flow into and out of the sampling manifold was constant at all times, and the magnitude of this flow was equal to the sum of each of the individual ozone instrument sampling flow rates.

The ozone generators were adjusted to bring the total ozone concentration in the sampling manifold to the desired level. No attempt was made to measure the amount of supplemental ozone added. It was important to incorporate this feature into the design of the sampling system in order to be able to achieve higher concentration levels for test purposes. In the event that higher levels would occur naturally, then adding ozone would not be required. The site could be anticipated to experience ozone levels perhaps as high as 0.2 ppm under usual circumstances at this time of the year. Concentrations between 0.2 to 0.5 ppm could probably be achieved only by adding supplemental ozone. The quantity of air through the ozone generation system was kept low in order to minimize dilution of other interfering substances present in ambient air.

No problems were encountered in this mode of operation, and the sampling system performed satisfactorily in every respect.

2. Phase II (Bias)

It was necessary to have known values of samples in order to evaluate the bias or accuracy of the test method. These known values were obtained from calibrated ozone generating equipment furnished by the National Bureau of Standards (NBS). A set of generating equipment was supplied to each collaborator, and the specified measurements of ozone samples were made by the collaborator at his own location.

A schematic diagram of the ozone generating system is shown in Figure 2. The equipment between the dotted lines was constructed and supplied by NBS. The filter contains charcoal to remove hydrocarbons and nitrogen dioxide, and a molecular sieve to remove water.

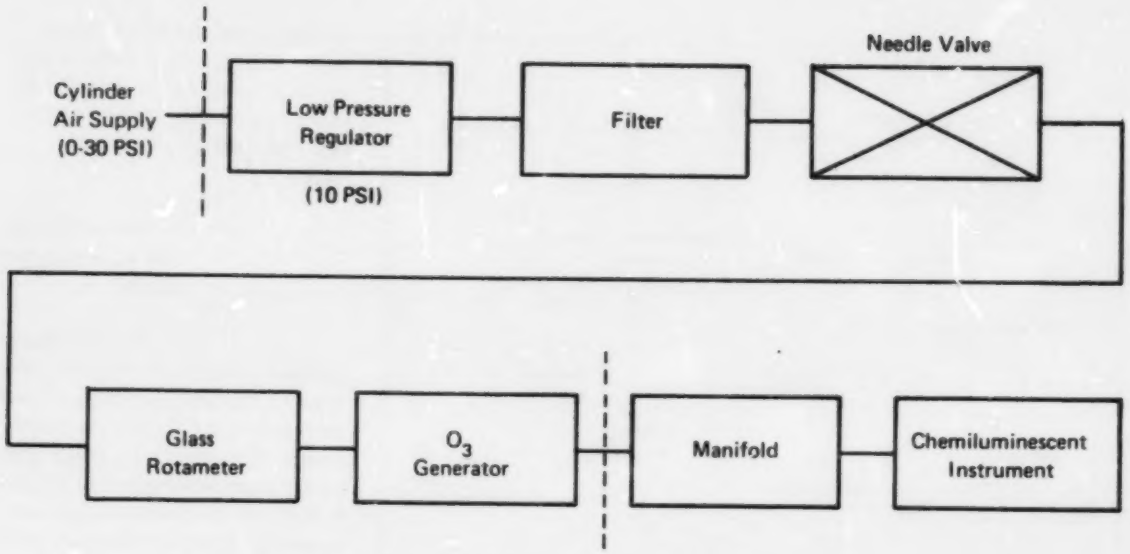

FIGURE 2. SIMPLIFIED EQUIPMENT CONNECTION DIAGRAM
(Phase II)

Each ozone generator was calibrated by NBS as a unit using its specifically designated power supply, air regulator and rotameter. The ozone concentrations produced by each generator were compared at several shutter settings with the ozone produced by a standard generator using a chemiluminescent ozone analyzer as a comparator.

The standard generator was initially calibrated by the 1.0% neutral buffered potassium iodide method (NBKI). The generator was then used to generate NO_2 by gas phase titration (GPT) of NO ($NO + O_3 \rightarrow NO_2 + O_2$) where the concentration of NO_2 produced was based on the O_3 concentration determined by NBKI. The response of the NO_2 produced by GPT was then measured with a chemiluminescent NO_2 instrument that had been calibrated with a gravimetrically calibrated NO_2 permeation device (NBS Standard Reference Material 1629). Over the range 0.1 to 0.8 ppm NO_2, the response to the two sources of NO_2 was identical, within experimental error. Thus, the accuracy of the O_3 concentration produced by the standard is related to the accuracy of the permeation device (±2%) and is independent of the NBKI method.

The flow rate through the systems was approximately 5 liters per minute. The flow rate (to maintain calibrations) for each individual set of generating equipment was marked in red on the rotameter. The generator output was corrected to 760 mm of mercury and 25°C. The individual collaborators then corrected for the deviation of ambient temperatures and pressures from the standard. The range of reported temperature was from 20-29.8°C, and the range of atmospheric pressure was from 731-765.8 mm of mercury.

The calibrated generator, pressure regulator, filter, rotameter and fittings were supplied as a unit in order to maintain control over the system as a "standard". The collaborator had only to connect the air cylinder and adjust the pressure and flow rate to the indicated level. Temperature and pressure measurements were made by the collaborator during the test and recorded. The volume of air sampled by the collaborators was then adjusted by taking into account the pressure and temperature reference conditions at the time of calibration, as specified by the method.

The ozone generators were the same type as were used in Phase I, and were capable of supplying ozone concentrations from zero to 0.500 ppm with precision and stability in this mode of operation. Instructions on the set up and operation of the generating equipment were sent to each collaborator. The before test calibration data for each of the systems is shown in Table I. From Table I, the average of each of the five concentration levels over all labs is; 0.054, 0.084, 0.131, 0.273, and 0.481 ppm.

TABLE I. CALIBRATION DATA (BEFORE TEST) OZONE BY LABORATORY BY CONCENTRATION LEVEL (PHASE II)

Laboratory Number	Ozone Concentration Level Number (ppm)				
	1	2	3	4	5
10	0.053	0.082	0.129	0.269	0.475
11	0.054	0.084	0.131	0.274	0.482
13	0.054	0.084	0.131	0.274	0.482
14	0.054	0.084	0.131	0.274	0.482
15	0.054	0.084	0.132	0.274	0.484
16	0.054	0.084	0.132	0.274	0.484
17	0.054	0.084	0.131	0.274	0.482
18	0.054	0.084	0.132	0.274	0.484
19	0.054	0.084	0.132	0.274	0.484
20	0.053	0.082	0.129	0.269	0.475
Average Over All Labs	0.054	0.084	0.131	0.273	0.481

TABLE II. COMPARISON OF RESULTS OF INITIAL AND FINAL CALIBRATION AT SHUTTER SETTING OF 90 (PHASE II)

Generator Number*	Initial (ppm of O_3)	Final (ppm of O_3)	Change in Percent
10	0.49	0.48	−2
11	0.49	0.46	−6
13	0.49	0.44	−10
14	0.48	0.48	0
15	0.45	0.45	0
16	0.53	0.53	0
17	0.48	0.48	0
18	0.48	0.48	0
19	0.50	0.43	−14

*Generator Number 20 was damaged in return shipment.

A comparison of the before and after calibration is given in Table II. Section IV, A. of this report contains a discussion of these results.

D. Collaborative Test Procedure

1. Phase I (Precision)

An immense amount of planning and coordination was required in order to conduct the test. Each participant was provided with rather detailed instructions regarding what was required. The responsibilities of a participant can be divided into four general areas which are (1) calibration work in his own laboratory prior to coming to the test site; (2) transfer of equipment to and from the test site; (3) activities at the test site; and (4) processing of data after return from the test site.

Four different types of chemiluminescent instruments were represented in the test and are listed in Table III. A cross-section of available instruments was desirable; however, it was not the purpose of the experiment to compare instruments from different manufacturers. Because of the different instruments used in the test, it was impossible to give specific instructions applicable for all. The general recommendations to collaborators were to follow specific instructions given in the manufacturer's manual for the instrument, to make proper adjustments of flow controls and zero and span controls, and to record whatever parameters were necessary for future reference.

Each collaborator was instructed to perform all possible calibration procedures in his home laboratory as if the instrument was being prepared for placement at a monitoring site. Whatever supplemental calibration procedures (either recommended by the instrument manufacturer or considered necessary by the collaborator) that were essential were performed at the test site. Prior to coming to the test site, each collaborator was instructed to prepare a potassium iodide calibration curve according to Section 8.1 of the method (see method in Appendix). These data could be taken from an existing calibration curve then in use provided the curve was prepared in accordance with Section 8.1.1 and provided that actual data points could be reported. In other words, if a valid potassium iodide calibration curve was in use in a collaborator's laboratory, its use was permitted for the purposes of this test, and it was not necessary that another be prepared. It was not intended (but not precluded) that potassium iodide determinations be made at the test site; therefore, the essentials for that determination were made available at the test site should they be needed in any emergency case. The collaborators were instructed to transfer the instrument calibration reference points to the test site by proper standardization of internal or external ozone generators in order to minimize biasing the results. Calibration procedures were to cover the range 0 to .510 ppm (0 to 1000 $\mu g/m^3$) which is the range over which the precision information was desired. The reference points were not significantly changed by shipment.

Considerable effort was required by a collaborator to prepare, pack, and ship his equipment to and from the test site. Each collaborator was expected to bring the following items to the test site:

1. Chemiluminescent ozone monitor complete with sample ethylene and exhaust lines, connecting cables, and ethylene pressure regulator. An individual ethylene cylinder was provided for each collaborator at the test site.

2. Recorder complete with connecting cable, chart paper, ink supply, and appropriate chart speed motor, or gears to allow continuous recording for a period of five days.

3. Calibrated ozone generator (internal or external) with appropriate air filter, flowmeter, and air pump if required. Clean compressed air was available at the test site if necessary.

4. Miscellaneous tools to assemble and install equipment.

5. Other items considered necessary by the collaborator for the proper installation and operation of the ozone monitor.

TABLE III. LABORATORY INSTRUMENT TYPE AND METHOD OF CALCULATING HOURLY AVERAGES (Phase I)

Laboratory Number	Instrument Type	Method of Calculating Hourly Averages
1	Meloy	A line representing hourly average was visually constructed
2	McMillan	Obtained by area averaging method
3	Bendix	Visually constructed line of best fit
4	McMillan	Counting squares
5	Bendix	Taken by visual averaging of strip chart recording
6	REM	Trace, cut, and weigh
7	McMillan	Visual estimation of equal areas
8	Bendix	Planimeter
9	REM	Average of digital output

Upon arrival at the test site, the collaborator's first responsibility was to set up and check out his instruments. Connection of the intake and discharge lines from each of the instruments to the sample system was handled by Southwest Research Institute personnel. In general, there were no unusual problems; however, the instrument of one collaborator was damaged in shipment. At first it was believed that the instrument could not be brought into operation. However, a quick check indicated a broken electrical connection, a broken quartz tube in the ozone generator, and a bent fan cowl. Through the resources of the host, EPA personnel, Southwest Research Institute staff, and other collaborators, the instrument was repaired and in operation by mid-afternoon on Monday, the first day of the test. Though noisy, the instrument performed satisfactorily throughout the test. The test area was somewhat small and each collaborator was slightly crowded; however, no unusual problems were encountered. A partial view of the room and the sampling system is shown in Figure 3.

During the test period, a collaborator's responsibilities were generally limited to daily zero and span checks of his instrument, normally scheduled between 8 and 9 a.m. each morning of the test period. In general, a collaborator was present in the test area only during this time. All equipment was monitored by Southwest Research Institute personnel, and if a malfunction occurred, the respective collaborator was requested to come to the test site and make repairs. The only problems of this type occurring were an occasional failure of a recorder pen. These problems were not serious, and little or no data were lost as a result. The generation of test atmospheres did not require any action on the part of the collaborators. All atmospheres to be analyzed were passed through the manifold, and no collaborator action was required during the change from one mode of operation to another.

So far as the collaborators were concerned, there was no distinction between ambient atmospheres and ambient atmospheres containing supplemental ozone. In both cases, hourly averages were used.

Eash instrument was in continuous operation, and during the daylight hours was measuring ambient ozone concentrations. During the evening or nighttime hours, ozone supplemented atmospheres

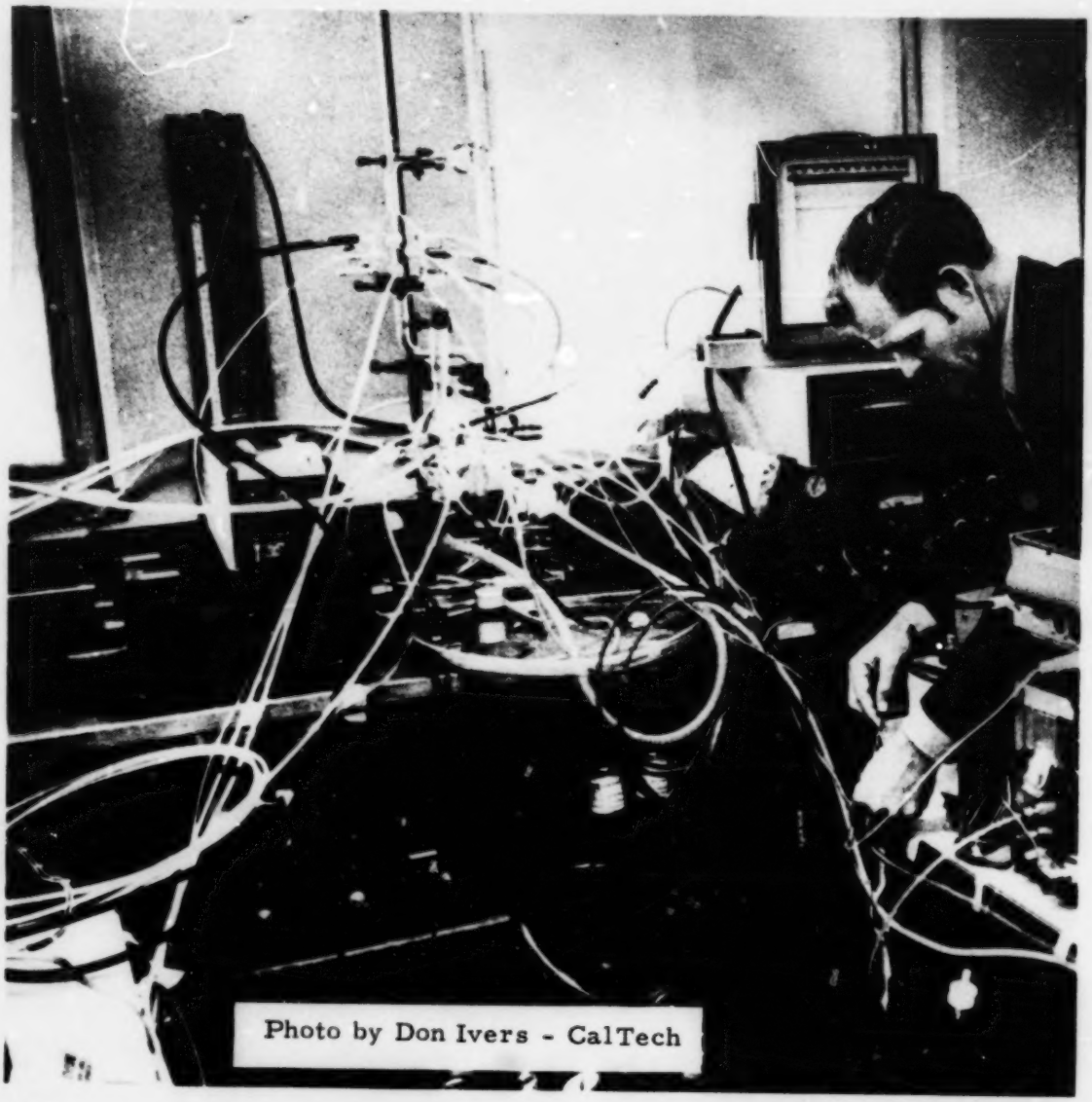

FIGURE 3. PARTIAL VIEW OF THE TEST AREA SHOWING SOME TYPICAL INSTRUMENTS AND THE SAMPLING SYSTEM (PHASE I)

were created and measured. On one night, the instruments measured ambient air all night long while supplemented atmospheres were measured during part or all of the remaining nighttime hours of the test.

Southwest Research Institute personnel assisted collaborators, and dismantled and packed the sampling system, and cleared and cleaned the test area.

The collaborators took their recorder charts home with them to await instructions for data processing and reporting. The data from the instrument operated by Southwest Research Institute as a collaborator was inspected, and a series of hourly periods for calculation of hourly averages was specified. These periods were to some extent randomly selected, excepting that they were usually specified between the hours or between the half hours. They were selected so that they did not encompass any step changes created as a result of changing from ambient atmospheres to supplemented atmospheres.

A detailed set of instructions and data forms was transmitted to each collaborator. These instructions were supplied to guide the collaborator through the preparation and submission of his report. Each observation to be reported was identified by the date and by start and finish times. A special data form greatly facilitated data reporting and handling.

There were 51 hourly averages specified for computation—32 for ambient and 19 for ozone supplemented samples. For these observations, the collaborator was instructed to report the hourly average between the times shown. The method allows the collaborator to use the averaging method of his choice; however, he was requested to report the method in detail. The various methods are indicated in Table III.

Collaborators were asked to report their results to the nearest 0.001 ppm if significant for their equipment. If this sensitivity was not obtainable with their system, they were requested to report less significant figures. They were asked not to report trailing zeros if their system was not capable of producing results to the nearest 0.001 ppm—for example, 0.07 should be reported instead of 0.070.

The collaborator's final report consisted of the following items:

1. Potassium iodide calibration curve. Submitted on a special form.

2. Instrument calibration curve. This curve was to reflect zero offset, if any, and sensitivity in terms of ppm per unit of instrument response so that Southwest Research Institute personnel would be able to interpret the analog records.

3. Collaborative testing data form. Collaborators were encouraged to make comments, to explain any unusual or atypical results, and to include notations regarding the individual results.

4. A description of the method of obtaining hourly averages.

5. Original analog records. The original chart records were requested, and any collaborator who wished to have these records returned after the completion of data analysis was asked to so specify.

6. Comments and criticisms. Collaborators were invited and encouraged to submit any such comments they felt important. Comments could involve the method, the equipment, the facilities provided, the instructions, or the manner in which the collaborative test was planned and conducted.

The collaborators apparently experienced no problems in interpretation of their analog records and calculation of average concentrations. Nine of the ten participating laboratories submitted results. As soon as results were received by Southwest Research Institute, they were screened for any unusual observations—that is, unusual in comparison with the results overall. In one or two instances, collaborators were asked to recalculate

one or more suspicious looking averages. The data were then coded into a computer compatible format and stored on the disc system of a time sharing computer service. This data file served as a basis for all subsequent statistical analysis.

2. Phase II (Bias)

Detailed instructions were provided to each collaborator on the test procedure. Portions of these instructions were unique to each collaborator (generator settings, concentration level, sampling order, etc.).

The following equipment was to be supplied by each collaborator:

a. Chemiluminescent ozone monitor complete with sample, ethylene, and exhaust lines; connecting cables; and ethylene pressure regulator and cylinder of ethylene.

b. Recorder complete with connecting cables, chart paper supply, ink supply, and appropriate chart motor speed.

c. Source of purified cylinder air for use with NBS calibrated ozone generator.

d. Absorbers, flowmeter, and spectrophotometer for potassium iodide determinations.

Each collaborator was required to perform the following functions, in accordance with the test procedure instructions and/or the test method:

a. Set up and operate the EPA supplied ozone generating equipment in accordance with the instructions provided with the equipment.

b. Prepare a curve of absorbance of various standard iodine solutions versus calculated ozone equivalents according to Section 8.1 of the Method (Appendix).

c. Each day of the test prepare a calibration curve of instrument response versus ozone concentration as determined by the KI method per Section 8.2 of the Method, utilizing the instrument manufacturer's instructions as necessary.

d. Sample and analyze the test atmospheres as per the test procedure instructions.

At the completion of the test, the collaborators were to submit a final report consisting of the following items:

a. Potassium iodide calibration curve.

b. Instrument calibration curve. This curve was to reflect zero offset, if any, and sensitivity in terms of ppm per unit of instrument response so that Southwest Research Institute personnel would be able to interpret the analog records.

c. Collaborative testing data form. Collaborators were encouraged to make comments, to explain any unusual or atypical results.

d. A description of the method of calculating hourly average ozone concentrations from the analog records.

e. Original analog records.

f. Comments and criticisms. Collaborators were invited and encouraged to submit any such comments they felt were important.

TABLE IV. LABORATORY INSTRUMENT TYPE AND METHOD OF CALCULATING HOURLY AVERAGES (PHASE II)

Laboratory Number	Instrument Type	Method of Calculating Hourly Responses
10	MEC	Visual averaging of hour readings
11	Bendix	Visual averaging of hour readings
13	Meloy	A straight line through chart response was visually constructed. Average values taken from midpoint of line.
14	MEC	Visual observation of strip chart reading for hourly run, subtraction of offset, and value entered on calibration curve and read off.
15	REM	Arithmetic average of 60 print-outs (one per minute) from recorder.
16	REM	Visual observation and averaging of hourly readings on chart records.
17	Bendix	Visual observation and averaging of hourly readings on chart records.
18	Bendix	Visual averaging the hourly readings on strip chart.
19	Bendix	Visual observation of the chart records.
20	Bendix	Visual estimating the average over the hour from the strip chart.

Table IV presents a list by laboratory number of instrument types and method of calculating hourly averages of concentration level measurements for those laboratories that completed the test.

III. STATISTICAL DESIGN AND ANALYSIS (PHASE I, PRECISION)

A. Design of Experiment

In collaborative testing, two general sources of variability can be readily detected. First, the variability between laboratories can be estimated. This is frequently the largest source of variability and is not under the control of the investigator. Second, the within-laboratory variability can be estimated. The separate sources which make up the within-laboratory variability cannot be estimated in this test. The separate sources are lumped into a single variable including the variability between days and the variability between replicates, neither of which can be individually defined.

In order to achieve the above goal, two distinct statistical analyses were used. The results of both were coordinated into what was believed to be the best description of the precision of the method.

The first method involves the computation of standard deviation for each respective sample. Each sample standard deviation provides an estimate of the total process variability at the sample concentration level, and includes both the between-laboratories and within-laboratory components. However, the first method yields no information regarding the within-laboratory or between-laboratories components of the total variance.[6]

The second method, the linear model analysis,[5] yielded estimates of the total standard deviation (S_T), between-laboratory standard deviation (S_L) and within-laboratory standard deviation (S_{WL}).

The linear model analysis also served as a good method in itself for detecting outliers. The method is described in detail in the respective reference, and the interested reader may consult that reference.

B. Results and Statistical Analysis

The data yielded by the experiment for ambient and supplemented atmospheres are tabulated in Table V. These data have been edited to the extent that only samples for which all laboratories were able to produce an observation are recorded. These data can be seen to consist for each laboratory of 29 observations for ambient atmospheres, and 19 observations for supplemented atmospheres. Several preliminary analyses were made to determine how the data might best be grouped for analysis. In this preliminary examination, the linear model analysis was applied to the ambient atmosphere data alone, to the supplemented atmosphere data alone, and to the ambient and supplemented atmosphere data combined. It resulted that the combination of ambient atmosphere data and supplemented atmosphere data would provide the best analysis. The results from the subsequent analysis reinforced this conclusion. These analyses also revealed three sample outliers and one laboratory outlier. These outliers may be observed by referring to Table V. In this table, the data are arranged in order of increasing sample means from top to bottom of the table and increasing laboratory means from left to right in the table. The high standard deviations for Samples 17 and 19 (lines 5 and 6 in the table) are obviously due to atypical results by Laboratory 3. The "studentized" ratio outlier test[7,8] was used, and individual observations in the body of the table are followed by a dagger if they are significant outliers ($\alpha = 0.05$) and an asterisk if they are highly significant outliers ($\alpha = 0.01$). The discarding of the two sample outliers does not cause any significant changes in results or interpretations because of the large number of valid data points which are still available. However, the rejection of Laboratory 9 deserves more careful consideration.

Further examination of the data for Laboratory 9 in Table V reveals a total of 13 outliers among the 48 samples. Five outliers occurred in the ambient sample data, and eight outliers occurred in the supplemented atmosphere data. (Sample Nos. 1 through 29 are ambient atmosphere data, and Sample Nos. 30 through 48 are supplemented atmosphere data.) The total number of outliers represents about 25 percent of the observations by this laboratory. Likewise, the overall average obtained by Laboratory 9 is an outlier with respect to the set of laboratory averages as shown at the bottom of the table. Two approaches were possible. The entire data for Laboratory 9 could be eliminated from the analysis, or every sample where an outlier is present could be elim-

TABLE V. AMBIENT AND SUPPLEMENTED OZONE ATMOSPHERES WITH OBSERVATIONS FOR EACH SAMPLE FOR EACH LABORATORY (PPM)

Rank	Sample	Laboratory Number									Mean	Std Dev
		9	5	7	8	6	4	3	1	2		
Ambient												
1	29	0.013*	0.000	0.000	0.000	0.000	−0.003	0.002	0.001	0.000	0.002	0.005
2	3	0.010	0.005	0.000	0.004	0.005	0.003	0.007	−0.005	0.005	0.004	0.005
3	18	0.003	0.005	0.005	0.002	0.005	0.007	0.008	0.006	0.005	0.005	0.002
4	2	0.021	0.015	0.001	0.014	0.015	0.013	0.017	0.007	0.015	0.013	0.006
5	19	0.003	0.010	0.010	0.008	0.012	0.011	0.035*	0.013	0.015	0.013	0.009
6	17	0.008	0.010	0.010	0.010	0.010	0.010	0.045*	0.008	0.015	0.014	0.012
7	4	0.019	0.022	0.024	0.030	0.025	0.026	0.027	0.029	0.025	0.025	0.004
8	28	0.022	0.030	0.033	0.028	0.029	0.030	0.037	0.033	0.040	0.032	0.005
9	1	0.035	0.032	0.020†	0.033	0.035	0.028	0.035	0.030	0.035	0.032	0.005
10	9	0.025	0.028	0.038	0.030	0.040	0.030	0.037	0.033	0.030	0.033	0.005
11	8	0.035	0.038	0.052	0.042	0.053	0.043	0.045	0.046	0.045	0.044	0.006
12	7	0.037	0.042	0.057	0.050	0.053	0.048	0.052	0.053	0.050	0.049	0.006
13	6	0.041	0.045	0.052	0.048	0.056	0.050	0.052	0.053	0.050	0.049	0.005
14	5	0.043	0.050	0.057	0.053	0.060	0.054	0.056	0.057	0.055	0.054	0.005
15	10	0.054	0.058	0.061	0.062	0.066	0.067	0.070	0.065	0.065	0.063	0.005
16	27	0.054	0.065	0.062	0.066	0.068	0.068	0.075	0.071	0.080	0.068	0.008
17	15	0.051†	0.068	0.070	0.065	0.072	0.070	0.075	0.070	0.075	0.068	0.007
18	20	0.066	0.070	0.075	0.071	0.073	0.072	0.075	0.073	0.080	0.073	0.004
19	26	0.064†	0.082	0.080	0.083	0.092	0.082	0.087	0.086	0.095	0.084	0.009
20	16	0.065†	0.082	0.080	0.085	0.095	0.086	0.090	0.088	0.090	0.085	0.009
21	11	0.075	0.080	0.080	0.085	0.097	0.088	0.081	0.090	0.090	0.085	0.007
22	21	0.078	0.085	0.090	0.087	0.090	0.084	0.080	0.089	0.095	0.087	0.005
23	22	0.085	0.095	0.099	0.100	0.105	0.100	0.100	0.102	0.110	0.099	0.007
24	12	0.085	0.100	0.094	0.101	0.108	0.099	0.102	0.104	0.110	0.100	0.008
25	25	0.091	0.105	0.100	0.111	0.117	0.110	0.107	0.112	0.130	0.109	0.011
26	24	0.094	0.110	0.108	0.112	0.120	0.115	0.115	0.117	0.125	0.113	0.009
32	14	0.115†	0.150	0.145	0.153	0.167	0.155	0.165	0.160	0.165	0.153	0.016
33	23	0.126	0.150	0.146	0.155	0.162	0.158	0.157	0.157	0.175	0.154	0.013
35	13	0.146	0.160	0.155	0.166	0.182	0.170	0.175	0.172	0.175	0.167	0.011
Supplemental Ozone Added												
27	37	0.077	0.122	0.151	0.150	0.123	0.155	0.142	0.172	0.150	0.138	0.028
28	36	0.077	0.122	0.156	0.148	0.125	0.154	0.140	0.173	0.150	0.138	0.028
29	38	0.087†	0.132	0.160	0.157	0.137	0.162	0.145	0.179	0.160	0.147	0.027
30	34	0.103	0.132	0.164	0.158	0.140	0.161	0.155	0.185	0.160	0.151	0.023
31	35	0.098†	0.135	0.164	0.160	0.145	0.162	0.155	0.182	0.165	0.152	0.024
34	39	0.111†	0.155	0.170	0.173	0.162	0.177	0.161	0.188	0.185	0.165	0.023
36	40	0.128*	0.168	0.179	0.181	0.183	0.184	0.182	0.190	0.195	0.176	0.020
37	42	0.140†	0.178	0.184	0.189	0.200	0.193	0.195	0.197	0.210	0.187	0.020
38	41	0.148†	0.180	0.188	0.192	0.203	0.197	0.197	0.203	0.215	0.191	0.019
39	46	0.229	0.262	0.258	0.278	0.272	0.289	0.285	0.280	0.310	0.274	0.023
40	47	0.248	0.278	0.272	0.291	0.292	0.290	0.307	0.289	0.330	0.289	0.023
41	48	0.254	0.285	0.277	0.297	0.298	0.295	0.310	0.293	0.340	0.294	0.023
42	43	0.254	0.298	0.348	0.346	0.310	0.359	0.327	0.392	0.365	0.333	0.041
43	33	0.280	0.322	0.343	0.348	0.347	0.358	0.355	0.390	0.365	0.345	0.031
44	44	0.285	0.325	0.353	0.369	0.342	0.378	0.355	0.401	0.390	0.355	0.035
45	32	0.298	0.345	0.362	0.365	0.377	0.373	0.382	0.406	0.390	0.366	0.031
46	31	0.317†	0.362	0.377	0.381	0.400	0.387	0.395	0.417	0.405	0.383	0.030
47	30	0.319†	0.368	0.390	0.386	0.427	0.392	0.405	0.421	0.405	0.390	0.032
48	45	0.320	0.370	0.382	0.407	0.410	0.414	0.420	0.429	0.445	0.400	0.038
Average		0.111†	0.132	0.139	0.142	0.144	0.145	0.146	0.152	0.154	0.141	0.013
Std Dev		0.096	0.111	0.117	0.120	0.120	0.123	0.121	0.131	0.130	0.119	

*Outlier, significant at $\alpha = 0.01$.
†Outlier, significant at $\alpha = 0.05$.

inated from the analysis, or every sample where an outlier is present could be eliminated from the analysis. In view of the fact that all but three outliers in the entire table occurred in Laboratory 9 data, it seemed most appropriate to delete Laboratory 9 data from all subsequent analyses. Therefore, all subsequent statistical analyses were made deleting Laboratory 9 and deleting Samples Nos. 17 and 19, leaving a total of eight laboratories and 46 samples. As graphic evidence of the appropriateness of this decision, Figure 4, which includes data from Laboratory 9 is presented. In this plot, each individual observation is plotted versus the respective average of each laboratory's observation for that sample. The numerals appearing in the plot represent the laboratory numbers. Where two or more observations fall in the same plotting position, an "x" appears. For further clarification, a line of slope = 1 has been superimposed on the plot. If agreement was perfect, all points would appear on this line. The relative departures of the data from Laboratory 9 are now clearly evident.

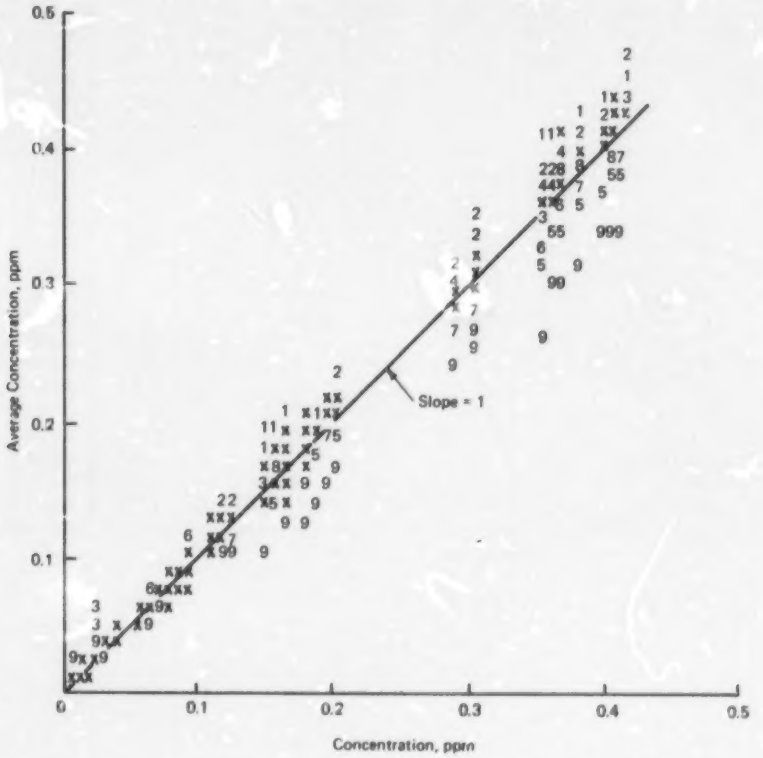

FIGURE 4. PLOT OF INDIVIDUAL OBSERVATIONS VERSUS OVERALL AVERAGE FOR EACH SAMPLE (Phase I)

Table VI is analogous to Table V and shows the corresponding results following the deletion of Laboratory 9 and Samples Nos. 17 and 19. Comparison of the standard deviations shown in these two tables reveals the degree of inflation of variances which would result if the data for Laboratory 9 were retained in the analysis.

Each of the standard deviations in Table V is an estimate of the total variability for the method. These standard deviations (S_{TD}) have been plotted versus their respective average concentration in Figure 5. This plot illustrates the relationship of the total standard deviation to concentration. Superimposed on the plot is the line of best fit, assuming a linear relationship and using the least squares method. The equation of this line is as follows:

$$S_{TD} = 0.0018 + 0.0542x \text{ concentration (ppm)} \quad (1)$$

TABLE VI. AMBIENT AND SUPPLEMENTED OZONE ATMOSPHERES WITH OBSERVATIONS FOR EACH SAMPLE FOR EACH LABORATORY, OMITTING LABORATORY 9 and SAMPLES 17 and 19 (PPM)

Rank	Sample	Laboratory Number								Mean	Std Dev
		5	7	8	6	4	3	1	2		
Ambient											
1	29	0.000	0.000	0.000	0.000	−0.003	0.002	0.001	0.000	0.000	0.002
2	3	0.005	0.000	0.004	0.005	0.003	0.007	−0.005	0.005	0.003	0.004
3	18	0.005	0.005	0.002	0.005	0.007	0.008	0.006	0.005	0.006	0.002
4	2	0.015	0.001	0.014	0.015	0.013	0.017	0.007	0.015	0.012	0.005
5	4	0.022	0.024	0.030	0.025	0.026	0.027	0.029	0.025	0.026	0.003
6	1	0.032	0.020†	0.033	0.035	0.028	0.035	0.030	0.035	0.031	0.005
7	28	0.030	0.033	0.028	0.029	0.030	0.037	0.033	0.040	0.033	0.004
8	9	0.028	0.038	0.030	0.040	0.030	0.037	0.033	0.030	0.033	0.005
9	8	0.038	0.052	0.042	0.053	0.043	0.045	0.046	0.045	0.045	0.005
10	7	0.042	0.057	0.050	0.053	0.048	0.052	0.053	0.050	0.050	0.005
11	6	0.045	0.052	0.048	0.056	0.050	0.052	0.053	0.050	0.051	0.004
12	5	0.050	0.057	0.053	0.060	0.054	0.056	0.057	0.055	0.056	0.003
13	10	0.058	0.061	0.062	0.066	0.067	0.070	0.065	0.065	0.064	0.004
14	27	0.065	0.062	0.066	0.068	0.068	0.075	0.071	0.080	0.069	0.006
15	15	0.068	0.070	0.065	0.072	0.070	0.075	0.070	0.075	0.070	0.004
16	20	0.070	0.075	0.071	0.073	0.072	0.075	0.073	0.080	0.073	0.003
17	26	0.082	0.080	0.083	0.092	0.082	0.087	0.086	0.095	0.086	0.005
18	11	0.080	0.080	0.085	0.097	0.088	0.081	0.090	0.090	0.086	0.006
19	16	0.082	0.080	0.085	0.095	0.086	0.090	0.088	0.090	0.087	0.005
20	21	0.085	0.090	0.087	0.090	0.084	0.080	0.089	0.095	0.088	0.005
21	22	0.095	0.099	0.100	0.105	0.100	0.100	0.102	0.110	0.101	0.005
22	12	0.100	0.094	0.101	0.108	0.099	0.102	0.104	0.110	0.103	0.005
23	25	0.105	0.100	0.111	0.117	0.110	0.107	0.117	0.130	0.112	0.009
24	24	0.110	0.108	0.112	0.120	0.115	0.115	0.117	0.125	0.115	0.006
29	23	0.150	0.146	0.155	0.162	0.158	0.157	0.157	0.175	0.158	0.009
30	14	0.150	0.146	0.153	0.167	0.155	0.165	0.160	0.165	0.158	0.008
32	13	0.160	0.155	0.166	0.182	0.170	0.175	0.172	0.175	0.169	0.009
Supplemental Ozone Added											
25	37	0.122	0.151	0.150	0.123	0.155	0.142	0.172	0.150	0.145	0.017
26	36	0.122	0.156	0.148	0.125	0.154	0.140	0.173	0.150	0.146	0.017
27	38	0.132	0.160	0.157	0.137	0.162	0.145	0.179	0.160	0.154	0.015
28	34	0.132	0.164	0.158	0.140	0.161	0.155	0.185	0.160	0.157	0.016
31	35	0.135	0.164	0.160	0.145	0.162	0.155	0.182	0.165	0.159	0.014
33	39	0.155	0.170	0.173	0.162	0.177	0.161	0.188	0.185	0.171	0.012
34	40	0.168	0.179	0.181	0.183	0.184	0.182	0.190	0.195	0.183	0.008
35	42	0.178	0.184	0.189	0.200	0.193	0.195	0.197	0.210	0.193	0.010
36	41	0.180	0.188	0.192	0.203	0.197	0.197	0.203	0.215	0.197	0.011
37	46	0.262	0.258	0.278	0.272	0.289	0.285	0.280	0.310	0.279	0.016
38	47	0.278	0.272	0.291	0.292	0.290	0.307	0.289	0.330	0.294	0.018
39	48	0.285	0.277	0.297	0.298	0.295	0.310	0.293	0.340†	0.299	0.019
40	43	0.298	0.348	0.346	0.310	0.359	0.327	0.392	0.365	0.343	0.031
41	33	0.322	0.343	0.348	0.347	0.358	0.355	0.390	0.365	0.353	0.019
42	44	0.325	0.353	0.369	0.342	0.378	0.355	0.401	0.390	0.364	0.026
43	32	0.345	0.362	0.365	0.377	0.373	0.382	0.406	0.390	0.375	0.018
44	31	0.362	0.377	0.381	0.400	0.387	0.395	0.417	0.405	0.391	0.017
45	30	0.368	0.390	0.386	0.427	0.392	0.405	0.421	0.405	0.399	0.019
46	45	0.370	0.382	0.407	0.410	0.414	0.420	0.429	0.445	0.410	0.024
Average		0.137	0.145	0.148	0.149	0.151	0.151	0.159	0.160	0.150	0.007
Std Dev		0.111	0.116	0.120	0.120	0.122	0.121	0.130	0.129	0.121	

†Outlier, significant at $\alpha = 0.05$.

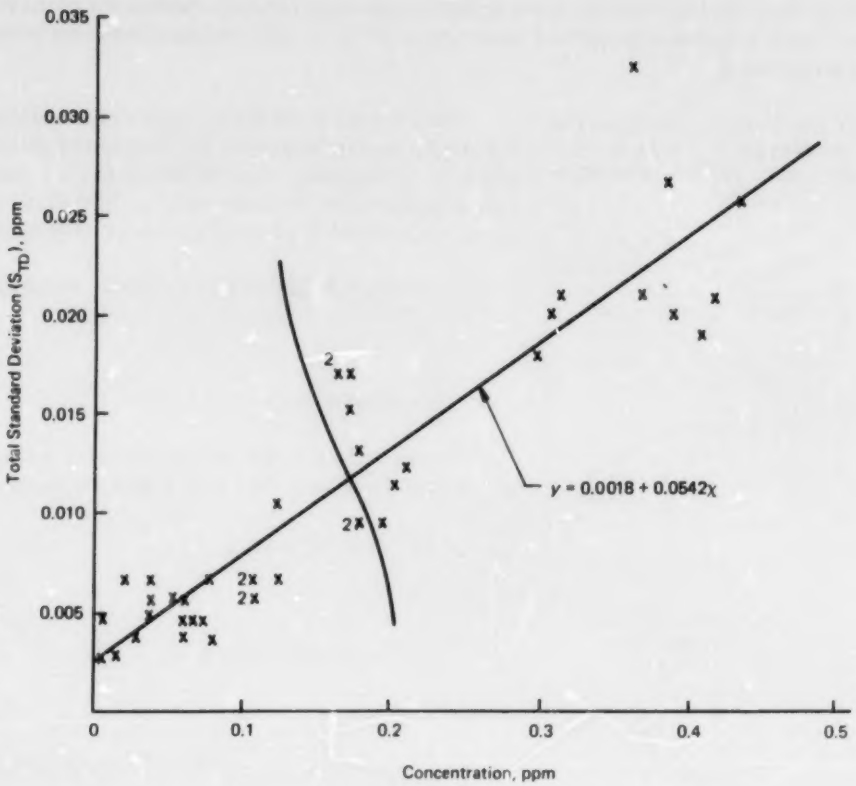

FIGURE 5. INDIVIDUAL ESTIMATES OF TOTAL STANDARD DEVIATION (S_{TD}) VERSUS CONCENTRATION (Phase I)

With the possible exception of the assumption of linearity, this line represents a perfectly valid estimate of the total standard deviation of the method; however, this analysis reveals no information whatsoever regarding the within-laboratory standard deviation (S_{WL}) or the between-laboratory standard deviation (S_L) of the method.

The within-laboratory standard deviation and the between-laboratory standard deviation for ambient air samples cannot be directly determined. However, because the ambient air quality standard calls for a one-hour average of not more than 0.08 ppm, it is important that a valid estimation of the within-laboratory and between-laboratory standard deviations of the method in this range be obtained.

In order to accomplish this objective, an appropriate transformation must be indirectly determined since the replication error for the ambient air data cannot be shown to vary with concentration. An appropriate transformation for the ozone supplemented atmosphere data was sought by a trial and error method. The type of transformation sought was of the type in Equation 2 below where a and b are the intercept and slope of the line of best fit of replication error versus concentration.

$$z = k\,[\ln(a + b\,y)] - G \qquad (2)$$

The details and techniques of this transformation are described in detail by Mandel.[5] The constants k and G are arbitrary, but it is useful if they can be selected so that the transformed data have the same range as the original data. The technique was to determine k and G so that at $y = 0$, $z = 0$ and at $y = 0.510$ ppm, $z = 0.510$ ppm; therefore, k and G are directly related to a and b. After each trial, the reproducibility was compared graphically with the

line of best fit for the individual estimates, and if satisfactory agreement was not obtained the constants a and b in Equation 2 were changed and another trial made. After five or six trials, adequate agreement between the two methods was obtained.

TABLE VII. MEANS, SLOPES, AND STANDARD ERRORS OF ESTIMATE FOR LINEAR MODEL ANALYSIS WITH DATA TRANSFORMATION (PHASE I)

Laboratory Number	Mean	Slope	Std. Error of Estimate
5	0.2064	0.9513	0.0071
7	0.2138	0.9855	0.0100
8	0.2168	0.9993	0.0044
4	0.2190	1.0137	0.0050
6	0.2193	0.9797	0.0115
3	0.2203	0.9891	0.0066
1	0.2257	1.0473	0.0110
2	0.2281	1.0341	0.0076
Average	0.2189	1.0000	0.0089*

*Pooled Estimate.

TABLE VIII. SUMMARY OF VARIANCE COMPONENTS FOR LINEAR MODEL ANALYSIS WITH DATA TRANSFORMATION (PHASE I)

Component	Value
Between Laboratories	
$V(\mu)$	0.0867
$V(\beta)$	44.57×10^{-8}
$V(\delta)$	12.09×10^{-8}
α	10.57×10^{-7}
z_0 (point of concurrence)	−0.0274
Within Laboratories	
$V(\lambda)$	0.04980
$V(\epsilon)$	0.07875
$V(\eta) = V(\lambda) + V(\epsilon)/\eta$	0.12855

Table VII shows the means, slopes and standard errors of estimate for each laboratory for the linear model analysis. Table VIII shows the summary of results for variance components and derived quantities for the linear model analysis. In all these tables, the data were transformed in accordance with Equation 3 below.

$$z = 0.31688\ [\ell_n(0.00255 + 0.02y) - \ell_n 0.00255] \qquad (3)$$

or

$$z = 0.31688\ \ell_n(1 + 7.843\,y) \qquad (3a)$$

The relationship of the standard deviation in the y scale to the standard deviation in the z scale is shown in Equation 4 below.

$$\sigma_y = \sigma_z\,(a + by)/kb \qquad (4)$$

or

$$\sigma_y = \sigma_z\,(0.4024 + 3.1558\,y), \qquad (4a)$$

where y is in ppm.

The concept of a test result[6] is incorporated, and a test result is defined as a single observation of an hourly average concentration. Following this concept, the four sources of variability as calculated by the linear model analysis for several values of concentration were tabulated. Table VIII shows these sources of variability and their relative importance as determined by the linear model analysis. The total variance in the z scale is shown along with the variance for each component and its respective percent of the total. The replication variance $V(\epsilon)$ is derived from the transformation parameters in accordance with Equation 5 below.

$$V(\epsilon) = (kb)^2 \qquad (5)$$

Comparison of $V(\epsilon)$ and $V(\lambda)$, the latter reflecting interferences in the method, reveals that they are approximately the same magnitude. Therefore, replication, even if possible, would not significantly improve the within-laboratory precision. The means and slopes from Table VII were shown to be correlated and therefore $V(\delta)$ appears in Table IX. This term, indicating the variability of the slopes of the laboratory lines, is negligible throughout the table. At concentrations below 0.15 ppm, the total variance is composed primarily of within-laboratory variation. The between-laboratory variation is relatively small in this range. At higher concentrations, the between-laboratory variability becomes more predominant, and at concentrations above 0.3 ppm, the between-laboratory variation accounts for more than one-half of the total variation.

For thoroughness, the analysis of variance table is shown in Table X, and from this, it can be shown that the laboratory lines have a tendency to intersect or concur at a particular point near the origin but, at that point, considerable scatter between the lines still exists. While this is of no direct importance to this study, it would have significance in the selection of standard samples for quality control in the use of the method.

TABLE IX. SOURCES OF VARIABILITY AND THEIR RELATIVE IMPORTANCE FOR THE LINEAR MODEL ANALYSIS WITH DATA TRANSFORMATION (PHASE I)

Y	Z	Within-Laboratory			%	Between-Laboratory			%	$V(Z)$
		$V(\epsilon)$	%	$V(\lambda)$		$(1+\alpha\gamma)^2 V(\mu)$	%	$\gamma^2 V(\delta)$		
0	0	40.2×10^{-6}	51.9	25.4×10^{-6}	32.8	0.5×10^{-6}	0.7	11.3×10^{-6}	14.6	77.5×10^{-6}
0.051	0.107	40.2×10^{-6}	49.2	25.4×10^{-6}	31.1	13.2×10^{-6}	16.1	3.0×10^{-6}	3.6	81.7×10^{-6}
0.102	0.186	40.2×10^{-6}	40.5	25.4×10^{-6}	25.6	33.3×10^{-6}	33.6	0.2×10^{-6}	0.3	99.2×10^{-5}
0.153	0.250	40.2×10^{-6}	32.9	25.4×10^{-6}	20.8	56.1×10^{-6}	46.0	0.2×10^{-6}	0.2	121.9×10^{-6}
0.204	0.303	40.2×10^{-6}	27.3	25.4×10^{-6}	17.3	79.6×10^{-6}	54.2	1.7×10^{-6}	1.1	146.9×10^{-6}
0.255	0.348	40.2×10^{-6}	23.3	25.4×10^{-6}	14.7	103.0×10^{-6}	59.7	4.0×10^{-6}	2.3	172.5×10^{-6}
0.306	0.388	40.2×10^{-6}	20.3	25.4×10^{-6}	12.8	125.9×10^{-6}	63.5	6.8×10^{-6}	3.4	198.2×10^{-6}
0.357	0.423	40.2×10^{-6}	18.0	25.4×10^{-6}	11.4	148.2×10^{-6}	66.3	9.9×10^{-6}	4.4	223.6×10^{-6}
0.408	0.455	40.2×10^{-6}	16.2	25.4×10^{-6}	10.2	169.8×10^{-6}	68.3	13.2×10^{-6}	5.3	248.6×10^{-6}
0.459	0.483	40.2×10^{-6}	14.7	25.4×10^{-6}	9.3	190.7×10^{-6}	69.9	16.7×10^{-6}	6.1	272.9×10^{-6}
0.510	0.510	40.2×10^{-6}	13.5	25.4×10^{-6}	8.6	210.9×10^{-6}	71.1	20.1×10^{-6}	6.8	296.6×10^{-6}

TABLE X. ANALYSIS OF VARIANCE TABLE FOR LINEAR MODEL ANALYSIS WITH DATA TRANSFORMATION (PHASE I)

Source	SS	DF	MS
Laboratories	$14,699.44 \times 10^{-6}$	7	$2,099.92 \times 10^{-6}$
Concentrations	$6,276,065.62 \times 10^{-6}$	45	$139,468.12 \times 10^{-6}$
Laboratory × Concentration	$25,449.50 \times 10^{-6}$	315	80.79×10^{-6}
Linear	$5,256.47 \times 10^{-6}$	7	750.92×10^{-6}
Concurrence	$4,139.75 \times 10^{-6}$	1	$4,139.75 \times 10^{-6}$
Non-Concurrence	$1,116.72 \times 10^{-6}$	6	186.12×10^{-6}
Deviation from Linearity	$20,192.48 \times 10^{-6}$	308	65.58×10^{-6}

F (Con./Non-Con.) = 22.243 Probability = 100
Point of Concurrence = −0.274
F (Non-Conc./Resid.) = 2,839 Probability = 99
Concurrence is not within experimental error.

TABLE XI. LISTING OF TOTAL, BETWEEN-LABORATORY, AND WITHIN-LABORATORY STANDARD DEVIATION DERIVED FROM LINEAR MODEL ANALYSIS* (PHASE I)

Z	$V(\eta)$	$V(Z)$	Y	S_{TM}	S_L	S_{WL}
0	65.6×10^{-6}	77.5×10^{-6}	0	0.0035	0.0012	0.0033
0.107	65.6×10^{-6}	81.7×10^{-6}	0.051	0.0051	0.0022	0.0046
0.186	65.6×10^{-6}	99.2×10^{-6}	0.102	0.0072	0.0041	0.0059
0.250	65.6×10^{-6}	121.9×10^{-6}	0.153	0.0098	0.0066	0.0072
0.303	65.6×10^{-6}	146.9×10^{-6}	0.204	0.0127	0.0094	0.0085
0.348	65.6×10^{-6}	172.5×10^{-6}	0.255	0.0159	0.0125	0.0098
0.388	65.6×10^{-6}	198.3×10^{-6}	0.306	0.0193	0.0157	0.0111
0.423	65.6×10^{-6}	223.7×10^{-6}	0.357	0.0229	0.0193	0.0124
0.455	65.6×10^{-6}	248.6×10^{-6}	0.408	0.0266	0.0228	0.0137
0.483	65.6×10^{-6}	272.9×10^{-6}	0.459	0.0306	0.0266	0.0150
0.510	65.6×10^{-6}	296.6×10^{-6}	0.510	0.0346	0.0305	0.0163

*S_{TM} – Total Standard Deviation, S_L – Between-Laboratory Standard Deviation, and S_{WL} – Within-Laboratory Standard Deviation.

Table XI presents a listing versus concentration level of the total standard deviation (S_{TM}), the between-laboratories standard deviation (S_L), and the within-laboratory standard deviation (S_{WL}). The concentration levels in the z transformation are given in ppm. The total standard deviation was calculated, using Equation 4a as follows:

$$S_{TM} = \sqrt{V(z)}\,(0.4024 + 3.1558\,y) \quad (6)$$

The within-laboratory standard deviation was calculated by the formula:

$$S_{WL} = \sqrt{V(\eta)}\,(0.4024 + 3.1558\,y) \quad (7)$$

Finally, the between-laboratories standard deviation was calculated as follows:

$$S_L = (S_{TM}^2 - S_{WL}^2)^{1/2} \quad (8)$$

In Figure 6, the calculated points from the linear analysis shown in Table XI for the total standard deviation (S_{TM}) are shown. In order to obtain a good fit of the regression line to these points, it was necessary to divide the line into two segments. The first segment is from 0 to 0.153 ppm and the other from 0.153 to 0.510 ppm. Also, on Figure 6, the S_{TD} regression line from Figure 5 is superimposed for comparison purposes. It is readily apparent that the results of the linear analysis agrees very well with the individual estimates of the total standard deviation over the entire range from 0 to 0.510 ppm.

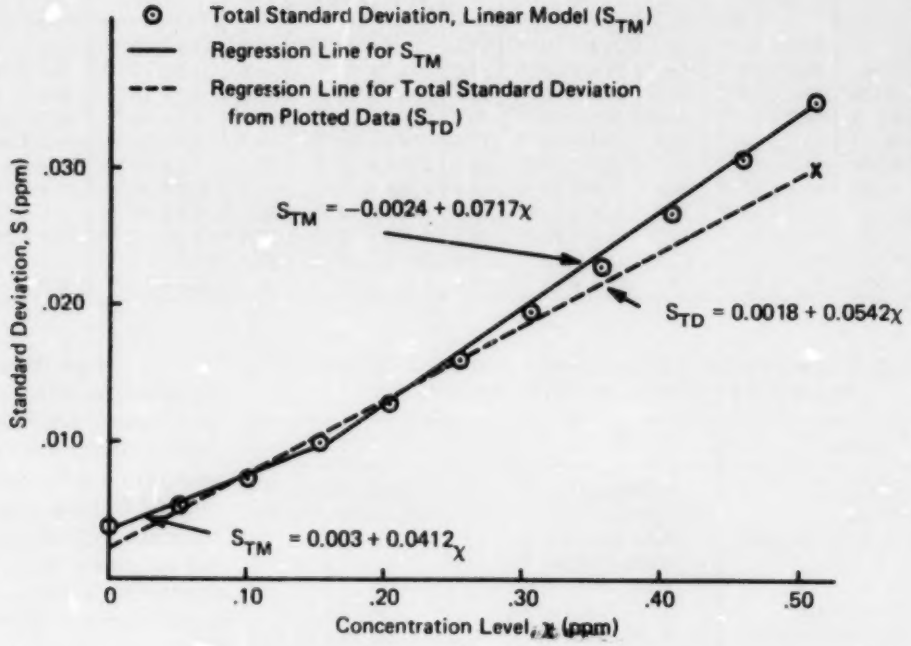

FIGURE 6. COMPARISON OF TOTAL STANDARD DEVIATION ESTIMATES VERSUS CONCENTRATION LEVEL FROM LINEAR MODEL AND DATA POINTS

Figure 7 presents the estimates of within-laboratory (S_{WL}) and between-laboratories (S_L) standard deviation. The regression line for S_L was divided into two segments for a better fit.

The equations for the estimate of the standard deviations versus concentration level (x) in ppm follow:

$$S_{TM} = 0.0033 + 0.0412x, \quad 0 < x \leq 0.153 \tag{9}$$

$$S_{TM} = -0.0024 + 0.0717x, \quad 0.153 < x \leq 0.510 \tag{9a}$$

$$S_L = 0.0008 + 0.0355x, \quad 0 < x \leq 0.153 \tag{10}$$

$$S_L = -0.0051 + 0.0690x, \quad 0.153 < x \leq 0.510 \tag{10a}$$

$$S_{WL} = 0.0033 + 0.0255x, \quad 0 < x \leq 0.510 \tag{11}.$$

Of particular interest is the lower detectable limit (*LDL*) of the concentration level. The *LDL* is often estimated using the standard deviations with a multiplier taken from the normal density function tables which encompasses a certain percentage of the area under the curve. For example, the value of 1.96 (from $-\infty$ to 1.96) encompasses 97.5% of the area. Thus, if the population of sampled values are normally distributed, and if the assumption is made that the estimate for the standard deviation is the true standard deviation, then when the estimate for the standard deviation is multiplied by 1.96, there is only a 2.5% risk that the *LDL* is greater than the product of 1.96 times the estimated standard deviation.

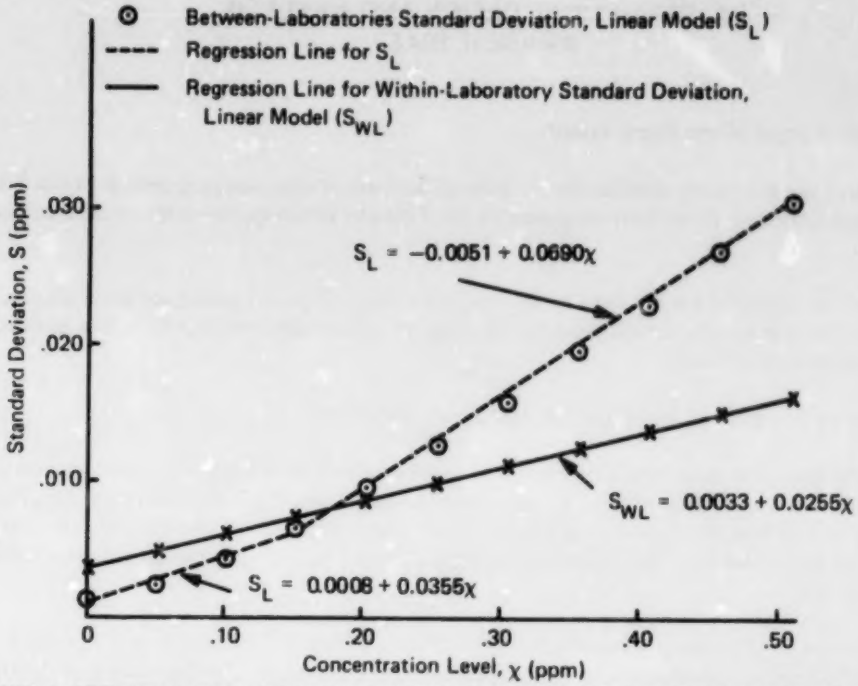

FIGURE 7. BETWEEN-LABORATORIES AND WITHIN-LABORATORY STANDARD DEVIATION ESTIMATES VERSUS CONCENTRATION LEVEL (DERIVED FROM LINEAR MODEL)

Applying this technique to the estimated standard deviations, the *LDL* for the three cases can be estimated.

1. The estimated *LDL*, taking into account the total standard deviation (using equation 9 with $x = 0$) is:

$$LDL(T) = (0.0033)(1.96) = 0.0065 \text{ ppm.}$$

2. The estimated *LDL* for between-laboratories (using equation 10) is:

$$LDL(L) = (0.0008)(1.96) = 0.0018 \text{ ppm.}$$

3. The estimated *LDL* for within-laboratory (equation 11) is:

$$LDL(WL) = (0.0033)(1.96) = 0.0062 \text{ ppm.}$$

IV. STATISTICAL DESIGN AND ANALYSIS (PHASE II, BIAS)

A. Purpose and Scope of the Experiment

The purpose of the test was to establish the accuracy of the method using sampling periods of one hour, to agree with the requirements of the ambient air quality standard thereby providing bias determination and quantification.

The scope of the experiment was limited by the time constraints inherent in taking one-hour samples. In order to solicit an adequate number of collaborators, the scope of the work involved was limited to an amount that could be accomplished in a week.

Each laboratory was required to analyze five separate concentrations.

Because individual ozone generating equipment was supplied to each laboratory, the concentrations were not identical for all laboratories. However, the deviation was less than 2 percent of the mean value for all laboratories for all five concentration levels at the calibration points. The expected mean concentrations were nominally 0.054, 0.084, 0.131, 0.273, and 0.481 parts per million (ppm). These values are taken as the true concentration levels at all laboratories.

The ozone generating equipment was calibrated by the National Bureau of Standards, and supplied to the collaborators. The calibration was checked by the National Bureau of Standards after the test was completed.

Table II shows the change in percent of the generator output at one setting (approximately at concentration level 5) from the first calibration. Generators 11, 13, and 19 showed a significant decline in output. A thorough check of the data points reported by these laboratories over the four days on which data was taken (see Table XII) did not show a pattern of decreasing amounts for each concentration level over the four days.

Referring to Table XVII, one sees that laboratories 13 and 19 display a higher average over all concentration levels than the overall average across all laboratories for all concentration levels. Thus it would appear that the generator output decline occurred after the measurements. Laboratory 11 had the lowest average of all the laboratories at four concentration levels. At concentration level 5, laboratory 11 had an average 44 percent below the overall average, and 29 percent below the next lowest average (laboratory 15). Thus, it seems improbable that the generator output decline contributed significantly to this effect. Therefore, no adjustment was made on the reported data for the differences in generator output before and after the test.

B. Design of the Experiment

The experiment was designed within the framework of the practical constraints of holding the collaborators' expected workload to a week. Within this constraint, the experiment was structured so that analysis of variance (ANOVA) techniques could be employed to obtain efficient estimates of the lower detectable limit.

The ANOVA techniques used in this study were:

1. A two-factor ANOVA with data in the original scale for each concentration level separately on data taken on the same day for concentration levels 1 and 5, and for the data taken across the three days for levels 1 through 5.

2. A linear model analysis[10] with data in the transformed scale.

TABLE XII. OBSERVED VALUES BY COLLABORATING LABORATORIES (PHASE II)

Laboratory Number	Ozone Concentration Level Number (ppm)						
	1		2	3	4	5	
	R	*D*	*D*	*D*	*D*	*R*	*D*
10	0.038	0.035	0.059	0.105	0.230	0.442	0.423
	0.037	0.038	0.065	0.106	0.237	0.440	0.430
	0.037	0.037	0.062	0.104	0.242	0.440	0.435
11	0.023	0.025	0.035	0.057	0.123	0.210	0.217
	0.020	0.023	0.033	0.055	0.120	0.210	0.213
	0.023	0.023	0.035	0.057	0.133	0.210	0.220
13	0.050	0.023	0.040	0.095	0.230	0.510	0.435
	0.055	0.015	0.040	0.090	0.230	0.505	0.440
	0.055	0.030	0.055	0.105	0.270	0.500	0.465
14	0.043	0.046	0.068	0.107	0.237	0.412	0.403
	0.043	0.044	0.067	0.107	0.235	0.386	0.404
	0.043	0.046	0.072	0.109	0.228	0.388	0.398
15	0.032	0.025	0.044	0.070	0.165	0.345	0.340
	0.032	0.032	0.065	0.087	0.203	0.323	0.357
	0.033	0.030	0.050	0.085	0.201	0.352	0.365
16	0.040	0.040	0.065	0.109	0.237	0.454	0.458
	0.042	0.041	0.063	0.106	0.236	0.454	0.448
	0.044	0.041	0.066	0.106	0.233	0.452	0.446
17	0.037	0.035	0.062	0.100	0.275	0.385	0.410
	0.037	0.030	0.052	0.090	0.210	0.383	0.370
	0.037	0.035	0.056	0.095	0.277	0.382	0.377
18	0.033	0.027	0.050	0.087	0.190	0.383	0.345
	0.032	0.035	0.058	0.100	0.220	0.378	0.399
	0.032	0.035	0.057	0.097	0.221	0.378	0.380
19	0.028	0.029	0.052	0.092	0.210	0.372	0.405
	0.030	0.035	0.060	0.100	0.226	0.368	0.420
	0.030	0.037	0.062	0.102	0.232	0.372	0.427
20	0.029	0.028	0.050	0.087	0.202	0.376	0.377
	0.027	0.030	0.052	0.091	0.208	0.368	0.391
	0.029	0.029	0.059	0.097	0.218	0.370	0.393

R–Replication (3 Readings at Concentration Levels 1 and 5 in One Day).
D–Day (One Reading at Each Concentration Level Per Day for Three Days).

The experimental design is shown in Figure 8. For the first ANOVA technique, each factor was represented in the following quantities:

1. Replicate data–laboratories (ten), replicates (three), with the replicates nested in the laboratories.

2. Data taken across days–laboratories (ten), days (three), with the days nested in the laboratories.

The data from the ten laboratories were analyzed with the second ANOVA technique with three days and five concentration levels. The linear model[5] views each of the five concentrations on each of the three days as individual materials. Thus, each of the laboratories has measured each of the 15 materials one time.

Referring to Figure 8, each laboratory made a total of 21 one-hour average determinations. For each of the first three days there were five separate concentration levels to be measured (levels 1 through 5), yielding a total of 15 determinations for the three days. On the fourth day, there were three sets of the first and fifth concentration levels to be measured, making a total of 6 determinations.

The order of the five concentration levels to be measured each day was randomized within and over all laboratories. The replication measurements of the first and fifth concentration levels on the fourth day were made alternately so that the error associated with setting the ozone generation slide scale would be incorporated in the replication error.

A detailed procedure was sent to each collaborator outlining the steps to be taken to carry out the necessary details of the test.

C. Preliminary Data Analysis

Only one of the eleven collaborators (laboratory number 12) was unable to conduct the series of tests because of reported ozone generating equipment problems. After several telephone conferences with the collaborator, it was decided to abort the test and return the equipment to NBS. The equipment was checked at NBS and found to be operating normally.

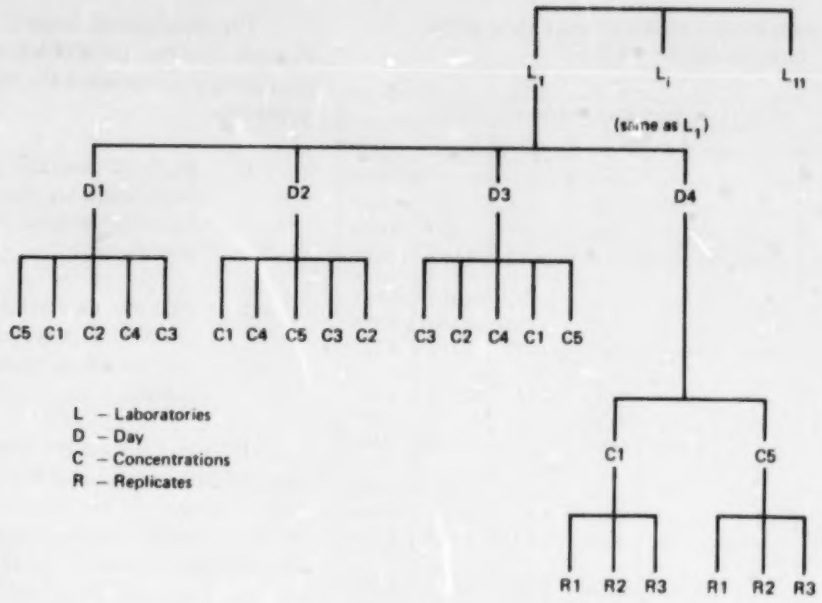

FIGURE 8. DESIGN OF OZONE METHOD TEST (Phase II)

The data provided by the other ten collaborators were checked to assure that the proper steps, as outlined in the method of converting the monitor graph plots to hourly averages of ozone readings in parts per million were accomplished. No obvious deviations from the prescribed method were noted. The calculations which were required by the method were checked for each collaborator, and only one inconsistency was found. One collaborator had failed to correct his monitor readings by the monitor calibration curves. These readings were corrected.

Several minor deviations from the test procedure were reported. These involved not following the prescribed concentration level order for the five daily measurements. One other deviation was the absence of one determination at a concentration level by a laboratory because of an inadvertent wrong setting on the generator slide scale. In this case, the average of the other two determinations was assumed, and the degrees of freedom was not adjusted since it would have only a minor effect on the overall analysis.

Overall, the response from the collaborators was very good, and from the review of the data submitted, it was apparent that each had worked conscientiously and diligently to conduct the test in accordance with the procedure and method.

D. Presentation of Data

The observed values recorded during the tests by each of the laboratories are listed in Table XII. The expected concentration values based on the calibrated ozone generating equipment are given in Table I, along with the averages of the expected concentration levels at each of the five points across all laboratories. The observed values were adjusted to compensate for the difference in the expected concentrations for the ten laboratories, and are displayed in Table XIII. The formula used to calculate the adjusted values (A) was:

$$A = O + (V - E),$$

where O is the observed value (from Table XII), V is the average value for a concentration level over all laboratories (from Table I), and E is the expected value for a concentration level for a laboratory (from Table I). In this manner, the data from each laboratory were adjusted to compensate for the minor variations in the standards across the laboratories, making it feasible to use the same expected value at a concentration level for all laboratories.

TABLE XIII. OBSERVED VALUES (ADJUSTED)
(PHASE II)

Laboratory Number	Ozone Concentration Level Number (ppm)						
	1		2	3	4	5	
	R	*D*	*D*	*D*	*D*	*R*	*D*
10	0.039	0.036	0.061	0.107	0.234	0.448	0.429
	0.038	0.039	0.067	0.106	0.241	0.446	0.436
	0.038	0.038	0.064	0.106	0.246	0.446	0.441
11	0.023	0.025	0.035	0.057	0.122	0.209	0.216
	0.020	0.023	0.033	0.055	0.119	0.209	0.212
	0.023	0.023	0.035	0.057	0.132	0.209	0.219
13	0.050	0.023	0.040	0.095	0.229	0.510	0.434
	0.055	0.015	0.040	0.090	0.229	0.505	0.439
	0.055	0.030	0.055	0.105	0.269	0.500	0.464
14	0.043	0.046	0.068	0.107	0.236	0.411	0.412
	0.043	0.044	0.067	0.107	0.234	0.415	0.386
	0.043	0.046	0.072	0.109	0.227	0.387	0.388
15	0.032	0.025	0.044	0.069	0.164	0.342	0.337
	0.033	0.032	0.065	0.086	0.202	0.320	0.354
	0.033	0.030	0.050	0.084	0.200	0.349	0.362
16	0.040	0.040	0.065	0.108	0.236	0.451	0.455
	0.042	0.041	0.063	0.105	0.235	0.451	0.445
	0.044	0.041	0.066	0.105	0.232	0.452	0.443
17	0.037	0.035	0.062	0.100	0.274	0.384	0.409
	0.037	0.030	0.052	0.090	0.209	0.382	0.369
	0.037	0.035	0.056	0.095	0.276	0.381	0.376
18	0.033	0.027	0.050	0.086	0.189	0.380	0.342
	0.032	0.035	0.058	0.099	0.219	0.375	0.396
	0.032	0.035	0.057	0.096	0.210	0.375	0.377
19	0.028	0.029	0.052	0.091	0.209	0.369	0.402
	0.030	0.035	0.060	0.099	0.225	0.365	0.417
	0.030	0.037	0.062	0.101	0.231	0.369	0.424
20	0.030	0.029	0.052	0.089	0.206	0.382	0.383
	0.028	0.031	0.054	0.093	0.212	0.374	0.397
	0.030	0.030	0.061	0.099	0.222	0.376	0.399

R–Replication (3 Readings at Concentration Levels 1 and 5 in One Day).
D–Day (One Reading at Each Concentration Level Per Day for Three Days).

Since the variance across the five concentration levels was not homogeneous, a transformation was necessary to establish homogeneity so the concentrations could be analyzed together. The transformed data appear in Table XIV.

E. Tests for Outlying Observations

A preliminary review of the data revealed that the observations reported by laboratory 11 were noticeably lower over concentration levels 2 through 5 than the observations reported by the other nine laboratories. Telephone discussions with the collaborator did not reveal any departure from the procedure or test method.

An analysis of variance was made on each concentration separately over all laboratories on the adjusted "day" data (Table XIII). From this analysis the variation within and between laboratories was obtained for each concentration level. Table XV is a summary of the analysis giving the cell average ($\bar{X}$), standard deviation (S) for each laboratory at each concentration level, as well as the within laboratory averages ($\bar{\bar{X}}$) and standard deviations (S_{WL}) for each concentration level.

Using the "Recommended Practice for Dealing With Outlying Observations" described in reference 9, a T' statistic was calculated for each cell average for the "day" data as follows:

$$T' = (\bar{\bar{X}} - \bar{X})/S_{\bar{X}},$$

where

$$S_{\bar{X}} = (S_{WL})/\sqrt{3}$$

This statistic (T') was then compared to a t value at the 99 percentile ($a = 0.01$) which was taken from Table 5 in reference 9, with $n = 10$.

$$t(0.01)(20df) = 3.37.$$

An a value of 0.01 was chosen to limit the probability of discarding valid data. All cell averages where T' is equal to or greater than t are considered to be potential outliers.

Table XVI presents the T' statistic for each laboratory at each level for the five concentration levels. Outliers are marked with an asterisk. Laboratory 11 displayed outliers at all five concentration levels. Only three laboratories had no outliers.

TABLE XIV. TRANSFORMED DATA (PHASE II)

Laboratory Number	Ozone Concentration Level Number (ppm)						
	1		2	3	4	5	
	R	*D*	*D*	*D*	*D*	*R*	*D*
10	0.093	0.087	0.135	0.205	0.338	0.475	0.465
	0.091	0.093	0.145	0.204	0.344	0.474	0.469
	0.091	0.091	0.140	0.204	0.348	0.474	0.471
11							
13	0.115	0.059	0.095	0.188	0.334	0.505	0.468
	0.124	0.040	0.095	0.181	0.334	0.502	0.470
	0.124	0.074	0.124	0.202	0.366	0.500	0.483
14	0.101	0.107	0.147	0.205	0.340	0.456	0.456
	0.101	0.103	0.145	0.205	0.338	0.441	0.442
	0.101	0.107	0.153	0.208	0.332	0.442	0.443
15	0.079	0.063	0.103	0.148	0.273	0.416	0.412
	0.081	0.078	0.142	0.175	0.310	0.402	0.423
	0.081	0.074	0.115	0.172	0.308	0.420	0.428
16	0.095	0.095	0.142	0.206	0.340	0.477	0.478
	0.099	0.097	0.138	0.202	0.339	0.477	0.473
	0.103	0.097	0.143	0.202	0.336	0.477	0.472
17	0.089	0.085	0.136	0.195	0.369	0.441	0.455
	0.089	0.074	0.118	0.181	0.316	0.440	0.423
	0.089	0.085	0.126	0.188	0.371	0.439	0.436
18	0.081	0.068	0.115	0.175	0.298	0.438	0.416
	0.079	0.085	0.129	0.194	0.325	0.436	0.447
	0.079	0.085	0.128	0.190	0.317	0.436	0.437
19	0.070	0.072	0.118	0.183	0.316	0.432	0.451
	0.074	0.085	0.133	0.194	0.331	0.430	0.459
	0.074	0.089	0.136	0.197	0.336	0.432	0.463
20	0.074	0.072	0.118	0.180	0.314	0.440	0.440
	0.070	0.077	0.122	0.185	0.319	0.435	0.448
	0.074	0.074	0.135	0.194	0.328	0.436	0.449

R–Replication (3 Readings at Concentration Levels 1 and 5 in One Day).
D–Day (One Reading at Each Concentration Level Per Day for Three Days).

An analysis of variance was then made on each concentration level separately over the remaining nine laboratories (excluding the data from laboratory 11). The laboratory standard deviation and cell averages remain the same, only the within laboratory standard deviation and concentration level average changes. These new values, with laboratory 11 data omitted are shown in the next to last row of Table XV. New values for T' were calculated and are shown in Table XVI. With laboratory 11 omitted, the critical value of $t(0.01)(18df)$ with $n = 9$ is 3.35. T' values which exceed t are marked with an asterisk. Of the remaining nine laboratories, six had one or more (three maximum) cells identified as potential outliers. It was obviously undesirable to drop all six laboratories from the study. Since no physical reason could be found for the outliers, it seemed plausible that the spread in the data may be a natural phenomenon associated with the test method, or nonconstant nonrandom differences between laboratories.

The linear model as described by Mandel[10] was utilized to investigate this possibility, since the linear model allows for nonconstant, nonrandom differences between laboratories. As a preliminary step[6], the data in Tables XVII and XVIII were tabulated. From Table XVIII, one sees that the ratio of the cell standard deviation to average standard deviation over all laboratories for a given laboratory does not fluctuate very much over all five concentration levels. However, the average of the ratios over the five concentration levels for each laboratory indicates there is a recognizable difference in the spread of the individual concentration measurement results between laboratories. The data in Table XVIII seem to support the probability of nonconstant, nonrandom differences between laboratories which, according to Mandel[10], is not an uncommon occurrence.

As a further check, a scale transformation of the data (see Table XIV) was made (to achieve homogeneity of variances) in accordance with the methods outlined by Mandel, and the linear model was exercised. The means, slopes, and standard error of the estimate are presented in Table XIX. None of the remaining 9 laboratories show values of both the mean and the slope that are much smaller than all the remaining laboratories. This fact indicates that no significant outliers exist in the data.

Another argument for not censoring all data points marked as potential outliers in Table XVI (with laboratory 11 censored) can be made. If laboratories 13 and 15 (each with 3 points marked as outliers) were censored from the

TABLE XV. WITHIN LABORATORY AND CELL MEANS AND STANDARD DEVIATION FOR FIVE CONCENTRATION LEVELS
(Adjusted Day and Replication Data)
Phase II

Laboratory Number	Parameter	Concentration Level (Day Data) (ppm)					Concentration Level Replication Data	
		1	2	3	4	5	1	2
10	$\bar{X}$	0.0377	0.0640	0.1063	0.2403	0.4353	0.0383	0.4467
	S	0.0015	0.0030	0.0006	0.0060	0.0060	0.0006	0.0012
11	$\bar{X}$	0.0237	0.0343	0.0563	0.1243	0.2157	0.0220	0.2090
	S	0.0012	0.0012	0.0012	0.0068	0.0035	0.0017	0.0000
13	$\bar{X}$	0.0227	0.0450	0.0967	0.2423	0.4457	0.0533	0.5050
	S	0.0075	0.0087	0.0076	0.0231	0.0161	0.0029	0.0050
14	$\bar{X}$	0.0453	0.0690	0.1077	0.2323	0.3953	0.0430	0.3943
	S	0.0012	0.0027	0.0012	0.0044	0.0145	0.0000	0.0145
15	$\bar{X}$	0.0290	0.0530	0.0797	0.1887	0.3510	0.0327	0.3370
	S	0.0036	0.0108	0.0093	0.0214	0.0128	0.0006	0.0151
16	$\bar{X}$	0.0407	0.0647	0.1064	0.2343	0.4510	0.0420	0.4512
	S	0.0006	0.0015	0.0017	0.0021	0.0069	0.0020	0.0006
17	$\bar{X}$	0.0333	0.0567	0.0950	0.2530	0.3847	0.0370	0.3823
	S	0.0029	0.0050	0.0050	0.0381	0.0214	0.0000	0.0015
18	$\bar{X}$	0.0323	0.0550	0.0937	0.2060	0.3717	0.0323	0.3767
	S	0.0046	0.0044	0.0068	0.0154	0.0274	0.0006	0.0029
19	$\bar{X}$	0.0337	0.0580	0.0970	0.2217	0.4143	0.0293	0.3677
	S	0.0042	0.0053	0.0053	0.0114	0.0112	0.0012	0.0023
20	$\bar{X}$	0.0300	0.0557	0.0937	0.2133	0.3930	0.0293	0.3773
	S	0.0010	0.0047	0.0050	0.0081	0.0087	0.0012	0.0042
Within labs (including 11)	$\bar{\bar{X}}$	0.0328	0.0555	0.0932	0.2156	0.3858	0.0359	0.3847
	S_{WL}	0.0035	0.0055	0.0275	0.0173	0.0146	0.0014	0.0071
Within labs (excluding 11)	$\bar{\bar{X}}$	0.0339	0.0579	0.0973	0.2258	0.4047	0.0375	0.4043
	S_{WL}	0.0037	0.0058	0.0055	0.0181	0.0154	0.0013	0.0074
Within labs (excluding 11, 13, 15)	$\bar{\bar{X}}$	0.0361	0.0604	0.0999	0.2287	0.4065	0.0359	0.3995
	S_{WL}	0.0027	0.0040	0.0043	0.0167	0.0156	0.0010	0.0059

data, the effects on the calculated accuracy (bias) of the method would be minimal, since from Table XVII we see that laboratory 13 has one of the higher averages over all concentration levels, and laboratory 15 has one of the lower averages.

The bias data for both cases (laboratory 11 censored, and laboratories 11, 13, and 15 censored) were calculated, and are shown in Table XX.

The T' statistic was also recalculated with laboratories 11, 13, and 15 censored. With seven laboratories,

$$t(0.01)(14df) = 3.33.$$

From Table XVI, there are still two potential outliers in laboratory 14, and one each in laboratories 16, 17, and 20.

Since it is undesirable to delete an individual concentration level data point for a laboratory (without deleting the entire laboratory data), and in view of the preceding arguments, it is felt that the inclusion of all the data from all laboratories except laboratory 11 in the analysis provided a realistic estimate of the accuracy (bias) of the method.

F. Accuracy (Bias) Determination

In order to determine the accuracy of the method, the standard error of the treatment means at each concentration level were used with the t distribution to calculate a 95% confidence interval on the mean at each concentration level, and also on the bias at each concentration level.

$$L_2 = \bar{\bar{X}} + 2.101\, S_{\bar{\bar{X}}}$$

The confidence limits were established on the concentration level means by the use of the relation:

$$L_1 = \bar{\bar{X}} - 2.101\, S_{\bar{\bar{X}}}$$

$$L_2 = \bar{\bar{X}} + 2.101\, S_{\bar{\bar{X}}}$$

where, L_1 and L_2 are the lower and upper limits, 2.101 is the value of the t distribution with 18 degrees of freedom that encompasses 95% of the area, $S_{\bar{\bar{X}}}$ is the standard error of the concentration level average ($S_{\bar{\bar{X}}} = S/\sqrt{3}$), and $\bar{\bar{X}}$ is the average over all laboratories for a concentration level. The parameters $\bar{X}$ and S are taken from Table XV. The confidence intervals on the means are shown in Figure 9.

TABLE XVI. T' STATISTIC FOR IDENTIFICATION OF POTENTIAL OUTLIERS

Concentration Level	Laboratories									
	10	11	13	14	15	16	17	18	19	20
All Laboratories										
1	2.39	4.53*	5.03*	6.18*	1.89	3.87*	0.25	0.25	0.24	0.41
2	2.65	6.59*	3.29	4.21*	0.79	2.86	0.36	0.32	0.77	0.04
3	4.34*	12.17*	1.14	4.78*	4.47*	4.22*	0.59	0.15	1.[illegible]	0.15
4	2.43	9.15*	2.67	1.67	2.70	1.87	3.74*	0.97	[illegible]	0.73
5	5.87*	20.16*	7.10*	1.13	4.12*	7.73*	0.13	1.67	[illegible]	0.86
Laboratory 11 Censored										
1	1.80		9.07*	5.42*	2.29	3.21	0.24	0.72	0.87	1.82
2	1.82		3.84*	3.31	1.46	2.02	0.37	0.86	0.03	0.66
3	2.83		0.20	3.25	5.52*	2.73	0.72	1.14	0.93	1.14
4	1.40		1.59	0.63	3.56*	0.82	2.61	1.90	0.39	1.19
5	3.45*		4.62*	1.39	6.05*	5.22*	2.25	3.72*	1.09	1.32
Laboratories 11, 13, and 15 Censored										
1	0.97			5.84*		2.88	1.79	2.42	1.57	3.90*
2	1.54			3.69*		1.83	2.05	2.34	1.04	2.05
3	2.59			3.13		2.62	1.97	2.51	1.17	2.51
4	1.21			1.46		2.26	2.52	2.36	0.73	1.60
5	3.20			1.16		4.62*	2.26	3.61*	0.82	1.40

*Potential Outliers

TABLE XVII. ADJUSTED DATA, LABORATORY AND CONCENTRATION LEVEL AVERAGES, AND STANDARD DEVIATION AVERAGE (PHASE II)

Laboratory Number	Concentration Level (ppm)					Laboratory Average Over All Concentration Levels
	1	2	3	4	5	
10	0.0377 0.0015	0.0640 0.0030	0.1063 0.0006	0.2403 0.0060	0.4353 0.0060	0.1767
13	0.0227 0.0075	0.0450 0.0087	0.0967 0.0076	0.2423 0.0231	0.4457 0.0161	0.1705
14	0.0453 0.0012	0.0690 0.0026	0.1077 0.0012	0.2323 0.0047	0.3953 0.0145	0.1699
15	0.0290 0.0036	0.0530 0.0108	0.0797 0.0093	0.1887 0.0214	0.3510 0.0128	0.1403
16	0.0407 0.0006	0.0647 0.0015	0.1060 0.0017	0.2343 0.0021	0.4510 0.0069	0.1793
17	0.0333 0.0029	0.0567 0.0050	0.0950 0.0050	0.2530 0.0381	0.3847 0.0214	0.1645
18	0.0323 0.0046	0.0550 0.0044	0.0937 0.0068	0.2060 0.0154	0.3717 0.0274	0.1517
19	0.0337 0.0042	0.0580 0.0053	0.0970 0.0053	0.2217 0.0114	0.4143 0.0112	0.1649
20	0.0300 0.0010	0.0557 0.0047	0.0937 0.0550	0.2133 0.0081	0.3930 0.0087	0.1571
Average of Averages	0.0339	0.0579	0.0973	0.2258	0.4047	0.1639
Average of Standard Deviations	0.0030	0.0051	0.0047	0.0145	0.0139	

TABLE XVIII. RATIOS OF STANDARD DEVIATIONS TO AVERAGE STANDARD DEVIATIONS OF CONCENTRATION LEVELS (PHASE II)

Laboratory Number	Concentration Level (ppm)					Average of Ratios
	1	2	3	4	5	
10	0.508	0.586	0.113	0.417	0.432	0.411
13	2.498	1.692	1.617	1.595	1.157	1.712
14	0.384	0.517	0.243	0.327	1.042	0.503
15	1.200	2.114	1.967	1.478	0.920	1.536
16	0.192	0.299	0.366	0.144	0.499	0.300
17	0.961	0.983	1.058	2.633	1.538	1.435
18	1.537	0.852	1.442	1.063	1.972	1.373
19	1.385	1.034	1.120	0.785	0.809	1.027
20	0.333	0.923	1.065	0.558	0.628	0.588

TABLE XIX. MEANS, SLOPES AND STANDARD ERRORS OF ESTIMATE FOR LINEAR MODEL ANALYSIS. DATA IN TRANSFORMED SCALE (PHASE II)

Laboratory Code No.	Mean	Slope	Standard Error of Estimate
15	0.215	0.9334	0.0067
18	0.227	0.9518	0.0023
20	0.231	0.9931	0.0027
13	0.235	1.1318	0.0072
19	0.238	1.0078	0.0029
17	0.238	1.0011	0.0148
14	0.249	0.9243	0.0011
10	0.251	1.0379	0.0033
16	0.251	1.0190	0.0060
Average	0.237	1.000	0.0070*

*Pooled Estimate

TABLE XX. 95% CONFIDENCE INTERVALS ON MEANS AND BIAS (PHASE II)

Concentration Level	True Value (μ)	Collab. Mean ($\bar{X}$)	Collab. Std. Err. Mean ($S_{\bar{X}}$)	95% Confidence Interval for Mean	Mean Percentage Difference	Difference ($\bar{X} - \mu$) Bias (B)	95% CI on B	95% CI on B as% of True Value
Laboratory 11 Censored (18 df)								
1	0.054	0.0339	0.0021	0.0294 to 0.0383	37	−0.0201	−0.0246 to −0.0157	−45 to −29
2	0.084	0.0579	0.0034	0.0508 to 0.0650	31	−0.0261	−0.0332 to −0.0191	−39 to −23
3	0.131	0.0973	0.0032	0.0906 to 0.1040	26	−0.0337	−0.0404 to −0.0270	−31 to −21
4	0.273	0.2258	0.0104	0.2039 to 0.2477	17	−0.0472	−0.0691 to −0.0253	−25 to −9
5	0.481	0.4047	0.0089	0.3860 to 0.4233	16	−0.0763	−0.0950 to −0.0577	−20 to −12
Laboratories 11, 13, and 15 Censored (14 df)								
1	0.054	0.0361	0.0016	0.0327 to 0.0395	33	−0.0179	−0.0212 to −0.0145	−39 to −26
2	0.084	0.0604	0.0023	0.0555 to 0.0654	28	−0.0236	−0.0285 to −0.0186	−33 to −22
3	0.131	0.0999	0.0025	0.0945 to 0.1052	24	−0.0311	−0.0364 to −0.0258	−28 to −20
4	0.273	0.2287	0.0096	0.2081 to 0.2493	16	−0.0443	−0.0649 to −0.0237	−24 to −8
5	0.481	0.4065	0.0090	0.3872 to 0.4257	15	−0.0745	−0.0951 to −0.0539	−20 to −11

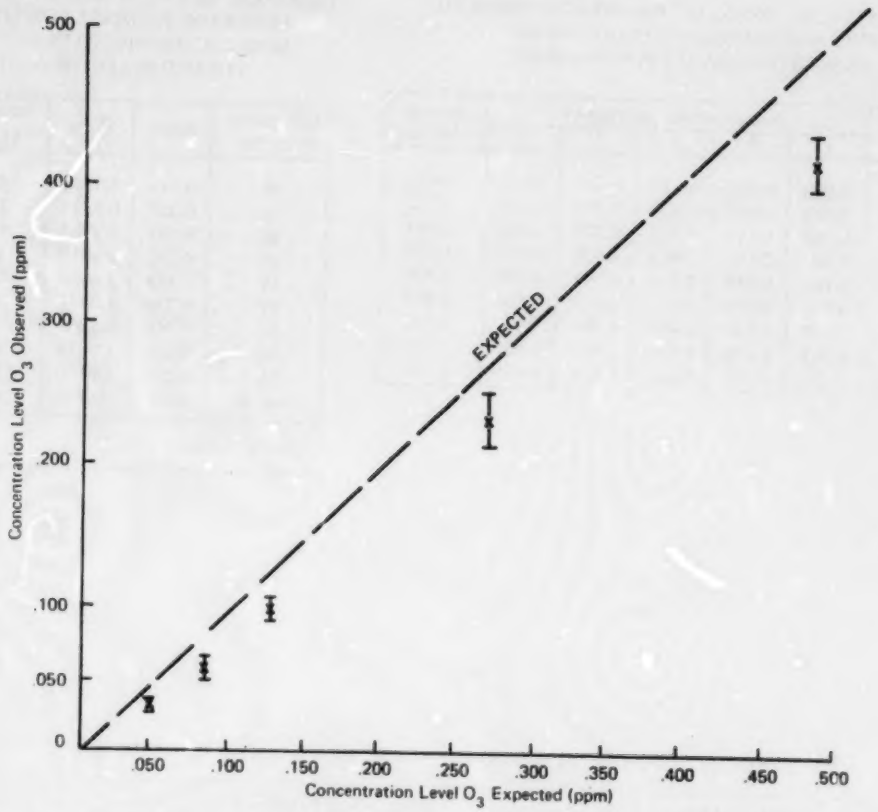

FIGURE 9. EXPECTED VERSUS AVERAGE OF OBSERVED VALUES (WITH 95% CONFIDENCE INTERVAL) FOR FIVE CONCENTRATION LEVELS (PHASE II) (Laboratory Eleven Censored)

The confidence limits on the bias[5] were calculated in a similar manner, with:

$$B = \bar{X} - \mu, \text{ and } S(B) = S_{\bar{X}}.$$

The confidence intervals on the bias estimate (B) were then calculated by replacing $\bar{X}$ with $\bar{X} - \mu$ in the formula previously given, where μ is the expected value for a concentration level taken from Table I. The results of these calculations are shown in Table XX. Figure 9 presents a plot of the average of the observed values, with the 95% confidence interval versus the expected values for the five concentration levels (with laboratory 11 censored).

G. Linear Model Analysis

A transformation of the data is necessary to make the variances be approximately homogeneous over the five concentration levels. The method advocated by Mandel[5] was chosen for the transformation. The transformation is of the form:

$$z = K \ln(A + By) - G, \text{ where}$$

$$A = 0.03047 \text{ and } B = 0.0317.$$

Setting $G = \ln A$, and applying the constraints:

when $y = 0, z = 0$ and

$y = 0.500, z = 0.500,$

then,

$$z = 0.274 \ln(0.03047 + 0.0317y) - \ln 0.03047$$

or

$$z = 0.274 \ln(1.0 + 10.4y),$$

where

y is the concentration level in parts per million. (13)

The transformed data are shown in Table XIV, and the means, slopes and standard error of the means are shown in Table XIX.

V. SUMMARY AND CONCLUSIONS

A. Phase I (Precision)

A measure of the precision of the Method is the relative magnitude of the variance components in the measuring process. Equations 1, 9, 9a, 10, 10a, and 11 are expressions for the various standard deviations as a function of concentration level, x (ppm).

$$S_{TD} = 0.0018 + 0.0542x \tag{1}$$

$$S_{TM} = 0.0033 + 0.0412x, \quad 0 < x \leq 0.153 \tag{9}$$

$$S_{TM} = -0.0024 + 0.0717x, \quad 0.153 < x \leq 0.510 \tag{9a}$$

$$S_{L} = 0.0008 + 0.0355x, \quad 0 < x \leq 0.153 \tag{10}$$

$$S_{L} = -0.0051 + 0.0690x, \quad 0.153 < x \leq 0.510 \tag{10a}$$

$$S_{WL} = 0.0033 + 0.0255x, \quad 0 < x \leq 0.510 \tag{11}.$$

The estimated LDL, using equation 9 with $x = 0$ is:

$$LDL(T) = 0.0033(1.96) = 0.0065 \text{ ppm.}$$

B. Phase II (Bias)

Over the range of 0 to 0.500 parts per million, a systematic negative bias exists in the Method. The upper limit of the 95% confidence interval on the observed average values of the concentration levels over all laboratories ranged from 9 to 29 percent below the true values, and the lower limit varied from 20 to 45 percent below the true values.

The mean percentage difference between the average observed value and the true value at the five concentration levels ranged from 15.9 to 37.3 percent.

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APPENDIX

REFERENCE METHOD FOR THE MEASUREMENT OF PHOTOCHEMICAL OXIDANTS CORRECTED FOR INTERFERENCES DUE TO NITROGEN OXIDES AND SULFUR DIOXIDE

Reproduced from Appendix D, "National Primary and Secondary Ambient Air Quality Standards," Federal Register, Vol. 36, No. 84, Part II, Friday, April 30, 1971

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8. *Calibration.*

8.1 *Calibration Curve.* Determine the linearity of the detector response at the operating flow rate and temperature. Prepare a calibration curve and check the curve furnished with the instrument. Introduce zero gas and set the zero control to indicate a recorder reading of zero. Introduce span gas and adjust the span control to indicate the proper value on the recorder scale (e.g. on 0–58 mg./m.³ scale, set the 46 mg./m.³ standard at 80 percent of the recorder chart). Recheck zero and span until adjustments are no longer necessary. Introduce intermediate calibration gases and plot the values obtained. If a smooth curve is not obtained, calibration gases may need replacement.

9. *Calculations.*

9.1 Determine the concentrations directly from the calibration curve. No calculations are necessary.

9.2 Carbon monoxide concentrations in mg./m.³ are converted to p.p.m. as follows:

$$\text{p.p.m. CO} = \text{mg. CO/m.}^3 \times 0.873$$

10. *Bibliography.*

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Jacobs, M. B. et al., *J.A.P.C.A. 9, No. 2,* 110–114, August 1959.

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ADDENDA

A. *Suggested Performance Specifications for NDIR Carbon Monoxide Analyzers:*

Range (minimum)	0–58 mg./m.³ (0–50 p.p.m.).
Output (minimum)	0–10, 100, 1,000, 5,000 mv. full scale.
Minimum detectable sensitivity.	0.6 mg./m.³ (0.5 p.p.m.).
Lag time (maximum)	15 seconds.
Time to 90 percent response (maximum).	30 seconds.
Rise time, 90 percent (maximum).	15 seconds.
Fall time, 90 percent (maximum).	15 seconds.
Zero drift (maximum)	3 percent/week, not to exceed 1 percent/24 hours.
Span drift (maximum)	3 percent/week, not to exceed 1 percent/24 hours.
Precision (minimum)	±0.5 percent.
Operational period (minimum).	3 days.
Noise (maximum)	±0.5 percent.
Interference equivalent (maximum).	1 percent of full scale.
Operating temperature range (minimum).	5–40° C.
Operating humidity range (minimum).	10–100 percent.
Linearity (maximum deviation).	1 percent of full scale.

B. *Suggested Definitions of Performance Specifications:*

Range—The minimum and maximum measurement limits.

Output—Electrical signal which is proportional to the measurement; intended for connection to readout or data processing devices. Usually expressed as millivolts or milliamps full scale at a given impedance.

Full Scale—The maximum measuring limit for a given range.

Minimum Detectable Sensitivity—The smallest amount of input concentration that can be detected as the concentration approaches zero.

Accuracy—The degree of agreement between a measured value and the true value; usually expressed as ± percent of full scale.

Lag Time—The time interval from a step change in input concentration at the instrument inlet to the first corresponding change in the instrument output.

Time to 90 percent Response—The time interval from a step change in the input concentration at the instrument inlet to a reading of 90 percent of the ultimate recorded concentration.

Rise Time (90 percent)—The interval between initial response time and time to 90 percent response after a step increase in the inlet concentration.

Fall Time (90 percent)—The interval between initial response time and time to 90 percent response after a step decrease in the inlet concentration.

Zero Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is zero; usually expressed as percent full scale.

Span Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is a stated upscale value; usually expressed as percent full scale.

Precision—The degree of agreement between repeated measurements of the same concentration, expressed as the average deviation of the single results from the mean.

Operational Period—The period of time over which the instrument can be expected to operate unattended within specifications.

Noise—Spontaneous deviations from a mean output not caused by input concentration changes.

Interference—An undesired positive or negative output caused by a substance other than the one being measured.

Interference Equivalent—The portion of indicated input concentration due to the presence of an interferent.

Operating Temperature Range—The range of ambient temperatures over which the instrument will meet all performance specifications.

Operating Humidity Range—The range of ambient relative humidity over which the instrument will meet all performance specifications.

Linearity—The maximum deviation between an actual instrument reading and the reading predicted by a straight line drawn between upper and lower calibration points.

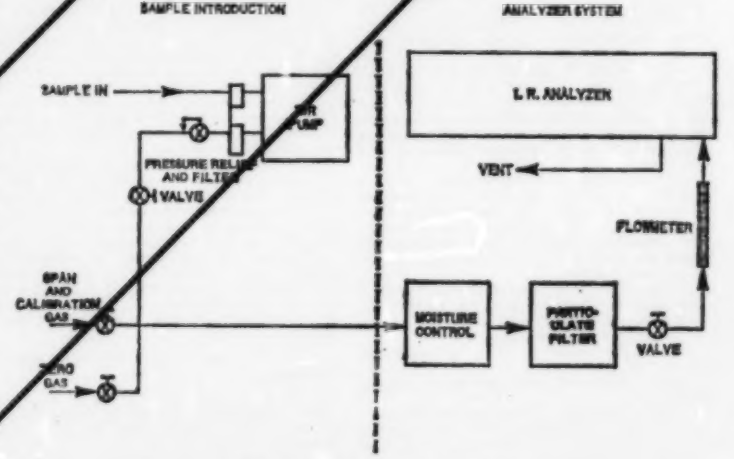

Figure C1. Carbon monoxide analyzer flow diagram.

APPENDIX D—REFERENCE METHOD FOR THE MEASUREMENT OF PHOTOCHEMICAL OXIDANTS CORRECTED FOR INTERFERENCES DUE TO NITROGEN OXIDES AND SULFUR DIOXIDE

1. *Principle and Applicability.*

1.1 Ambient air and ethylene are delivered simultaneously to a mixing zone where the ozone in the air reacts with the ethylene to emit light which is detected by a photomultiplier tube. The resulting photocurrent is amplified and is either read directly or displayed on a recorder.

1.2 The method is applicable to the continuous measurement of ozone in ambient air.

2. *Range and Sensitivity.*

2.1 The range is 9.8 μg. O_3/m.³ to greater than 1960 μg. O_3/m.³ (0.005 p.p.m. O_3 to greater than 1 p.p.m. O_3).

2.2 The sensitivity is 9.8 μg. O_3/m.³ (0.005 p.p.m. O_3).

3. *Interferences.*

3.1 Other oxidizing and reducing species normally found in ambient air do not interfere.

4. *Precision and Accuracy.*

4.1 The average deviation from the mean of repeated single measurements does not exceed 5 percent of the mean of the measurements.

4.2 The method is accurate within ±7 percent.

5. *Apparatus.*

5.1 *Detector Cell.* Figure D1 is a drawing of a typical detector cell showing flow paths of gases, the mixing zone, and placement of the photomultiplier tube. Other flow paths in which the air and ethylene streams meet

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at a point near the photomultiplier tube are also allowable.

5.2 *Air Flowmeter.* A device capable of controlling air flows between 0–1.5 l/min.

5.3 *Ethylene Flowmeter.* A device capable of controlling ethylene flows between 0–50 ml./min. At any flow in this range, the device should be capable of maintaining constant flow rate within ±3 ml./min.

5.4 *Air Inlet Filter.* A Teflon filter capable of removing all particles greater than 5 microns in diameter.

5.5 *Photomultiplier Tube.* A high gain low dark current (not more than 1×10^{-9} ampere) photomultiplier tube having its maximum gain at about 430 nm. The following tubes are satisfactory: RCA 4507, RCA 8575, EMI 9750, EMI 9524, and EMI 9536.

5.6 *High Voltage Power Supply.* Capable of delivering up to 2,000 volts of regulated power.

5.7 *Direct Current Amplifier.* Capable of full scale amplification of currents from 10^{-10} to 10^{-1} ampere; an electrometer is commonly used.

5.8 *Recorder.* Capable of full scale display of voltages from the DC amplifier. These voltages commonly are in the 1 millivolt to 1-volt range.

5.9 *Ozone Source and Dilution System.* The ozone source consists of a quartz tube into which ozone-free air is introduced and then irradiated with a very stable low pressure mercury lamp. The level of irradiation is controlled by an adjustable aluminum sleeve which fits around the lamp. Ozone concentrations are varied by adjustment of this sleeve. At a fixed level of irradiation, ozone is produced at a constant rate. By carefully controlling the flow of air through the quartz tube, atmospheres are generated which contain constant concentrations of ozone. The levels of ozone in the test atmospheres are determined by the neutral buffered potassium iodide method (see section 8). This ozone source and dilution system is shown schematically in Figures D2 and D3, and has been described by Hodgeson, Stevens, and Martin.

5.10 *Apparatus for Calibration.*

5.10.1 *Absorber.* All-glass impingers as shown in Figure D4 are recommended. The impingers may be purchased from most major glassware suppliers. Two absorbers in series are needed to insure complete collection of the sample.

5.10.2 *Air Pump.* Capable of drawing 1 liter/minute through the absorbers. The pump should be equipped with a needle valve on the inlet side to regulate flow.

5.10.3 *Thermometer.* With an accuracy of ±2° C.

5.10.4 *Barometer.* Accurate to the nearest mm. Hg.

5.10.5 *Flowmeter.* Calibrated metering device for measuring flow up to 1 liter/minute within ±2 percent. (For measuring flow through impingers.)

5.10.6 *Flowmeter.* For measuring airflow past the lamp; must be capable of measuring flows from 2 to 15 liters/minute within ±5 percent.

5.10.7 *Trap.* Containing glass wool to protect needle valve.

5.10.8 *Volumetric Flasks.* 25, 100, 500, 1000 ml.

5.10.9 *Buret.* 50 ml.

5.10.10 *Pipets.* 0.5, 1, 2, 3, 4, 10, 25, and 50 ml. volumetric.

5.10.11 Erlenmeyer Flasks. 300 ml.

5.10.12 *Spectrophotometer.* Capable of measuring absorbance at 352 nm. Matched 1-cm. cells should be used.

6. *Reagents.*

6.1 *Ethylene.* C. P. grade (minimum).

6.2 *Cylinder Air.* Dry grade.

6.3 *Activated Charcoal Trap.* For filtering cylinder air.

6.4 *Purified Water.* Used for all reagents. To distilled or deionized water in an all-glass distillation apparatus, add a crystal of potassium permanganate and a crystal of barium hydroxide, and redistill.

6.5 *Absorbing Reagent.* Dissolve 13.6 g. potassium dihydrogen phosphate (KH_2PO_4), 14.2 g. anhydrous disodium hydrogen phosphate (Na_2HPO_4) or 35.8 g. dodecahydrate salt ($Na_2HPO_4{\cdot}12H_2O$), and 10.0 g. potassium iodide (KI) in purified water and dilute to 1,000 ml. The pH should be 6.8±0.2. The solution is stable for several weeks, if stored in a glass-stoppered amber bottle in a cool, dark place.

6.6 *Standard Arsenious Oxide Solution (0.05 N).* Use primary standard grade arsenious oxide (As_2O_3). Dry 1 hour at 105° C. immediately before using. Accurately weigh to 2.4 g. the arsenious oxide from a small glass-stoppered weighing bottle. Dissolve in 25 ml. 1 N sodium hydroxide in a flask or beaker on a steam bath. Add 25 ml. 1 N sulfuric acid. Cool, transfer quantitatively to a 1,000-ml. volumetric flask, and dilute to volume. NOTE: Solution must be neutral to litmus, not alkaline.

$$\text{Normality } As_2O_3 = \frac{\text{wt. } As_2O_3 \text{ (g.)}}{49.46}$$

6.7 *Starch Indicator Solution (0.2 percent).* Triturate 0.4 g. soluble starch and approximately 2 mg. mercuric iodide (preservative) with a little water. Add the paste slowly to 200 ml. of boiling water. Continue boiling until the solution is clear, allow to cool, and transfer to a glass-stoppered bottle.

6.8 *Standard Iodine Solution (0.05 N).*

6.8.1 *Preparation.* Dissolve 5.0 g. potassium iodide (KI) and 3.2 g. resublimed iodine (I_2) in 10 ml. purified water. When the iodine dissolves, transfer the solution to a 500-ml. glass-stoppered volumetric flask. Dilute to mark with purified water and mix thoroughly. Keep solution in a dark brown glass-stoppered bottle away from light, and restandardize as necessary.

6.8.2 *Standardization.* Pipet accurately 20 ml. standard arsenious oxide solution into a 300-ml. Erlenmeyer flask. Acidify slightly with 1:10 sulfuric acid, neutralize with solid sodium bicarbonate, and add about 2 g. excess. Titrate with the standard iodine solution using 5 ml. starch solution as indicator. Saturate the solution with carbon dioxide near the end point by adding 1 ml. of 1:10 sulfuric acid. Continue the titration to the first appearance of a blue color which persists for 30 seconds.

$$\text{Normality } I_2 = \frac{\text{ml. } As_2O_3 \times \text{Normality } As_2O_3}{\text{ml. } I_2}$$

6.9 *Diluted Standard Iodine.* Immediately before use, pipet 1 ml. standard iodine solution into a 100-ml. volumetric flask and dilute to volume with absorbing reagent.

7. *Procedure.*

7.1 Instruments can be constructed from the components given here or may be purchased. If commercial instruments are used, follow the specific instructions given in the manufacturer's manual. Calibrate the instrument as directed in section 8. Introduce samples into the system under the same conditions of pressure and flow rate as are used in calibration. By proper adjustments of zero and span controls, direct reading of ozone concentration is possible.

8. *Calibration.*

8.1 *KI Calibration Curve.* Prepare a curve of absorbance of various iodine solutions against calculated ozone equivalents as follows:

8.1.1 Into a series of 25 ml. volumetric flasks, pipet 0.5, 1, 2, 3, and 4 ml. of diluted standard iodine solution (6.9). Dilute each to the mark with absorbing reagent. Mix thoroughly, and immediately read the absorbance of each at 352 nm. against unexposed absorbing reagent as the reference.

8.1.2 Calculate the concentration of the solutions as total $\mu g.\ O_3$ as follows:

$$\text{Total } \mu g.\ O_3 = (N)\ (96)\ (V_1)$$

N = Normality I_2 (see 6.8.2), meq./ml.

V_1 = Volume of diluted standard I_2 added, ml. (0.5, 1, 2, 3, 4).

Plot absorbance versus total $\mu g.\ O_3$.

8.2 *Instrument Calibration.*

8.2.1 *Generation of Test Atmospheres.* Assemble the apparatus as shown in Figure D3. The ozone concentration produced by the generator can be varied by changing the position of the adjustable sleeve. For calibration of ambient air analyzers, the ozone source should be capable of producing ozone concentrations in the range 100 to 1,000 $\mu g./m.^3$ (0.05 to 0.5 p.p.m.) at a flow rate of at least 5 liters per minute. At all times the airflow through the generator must be greater than the total flow required by the sampling systems.

8.2.2 *Sampling and Analyses of Test Atmospheres.* Assemble the KI sampling train as shown in Figure D4. Use ground-glass connections upstream from the impinger. Butt-to-butt connections with Tygon tubing may be used. The manifold distributing the test atmospheres must be sampled simultaneously by the KI sampling train and the instrument to be calibrated. Check assembled systems for leaks. Record the instrument response in nanoamperes at each concentration (usually six). Establish these concentrations by analysis, using the neutral buffered potassium iodide method as follows:

8.2.2.1 *Blank.* With ozone lamp off, flush the system for several minutes to remove residual ozone. Pipet 10 ml. absorbing reagent into each absorber. Draw air from the ozone-generating system through the sampling train at 0.2 to 1 liter/minute for 10 minutes. Immediately transfer the exposed solution to a clean 1-cm. cell. Determine the absorbance at 352 nm. against unexposed absorbing reagent as the reference. If the system blank gives an absorbance, continue flushing the ozone generation system until no absorbance is obtained.

8.2.2.2 *Test Atmospheres.* With the ozone lamp operating, equilibrate the system for about 10 minutes. Pipet 10 ml. of absorbing reagent into each absorber and collect samples for 10 minutes in the concentration range desired for calibration. Immediately transfer the solutions from the two absorbers to clean 1-cm. cells. Determine the absorbance of each at 352 nm. against unexposed absorbing reagent as the reference. Add the absorbances of the two solutions to obtain total absorbance. Read total $\mu g.O_3$ from the calibration curve (see 8.1). Calculate total volume of air sampled corrected to reference conditions of 25° C. and 760 mm. Hg. as follows:

$$V_s = V \times \frac{P}{760} \times \frac{298}{t+273} \times 10^{-3}$$

V_s = Volume of air at reference conditions, $m.^3$

V = Volume of air at sampling conditions, liters.

P = Barometric pressure at sampling conditions, mm. Hg.

t = Temperature at sampling conditions, °C.

10^{-3} = Conversion of liters to $m.^3$

Calculate ozone concentration in p.p.m. as follows:

$$\text{p.p.m. } O_3 = \frac{\mu g.\ O_3}{V_s} \times 5.10 \times 10^{-4}$$

8.2.3 *Instrument Calibration Curve.* Instrument response from the photomultiplier tube is ordinarily in current or voltage. Plot the current, or voltage if appropriate, (y-axis) for the test atmospheres against ozone concentration as determined by the neutral buffered potassium iodide method, in p.p.m. (x-axis).

9. *Calculations.*

9.1 If a recorder is used which has been properly zeroed and spanned, ozone concentrations can be read directly.

9.2 If the DC amplifier is read directly, the reading must be converted to ozone concentrations using the instrument calibration curve (8.2.3).

9.3 Conversion between p.p.m. and $\mu g./m.^3$ values for ozone can be made as follows:

$$\text{p.p.m. } O_3 = \frac{\mu g.\ O_3}{m.^3} \times 5.10 \times 10^{-4}$$

10. *Bibliography.*

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Nederbragt, G. W., Van der Horst, A., and Van Duijn, J., *Nature 206*, 87 (1965).

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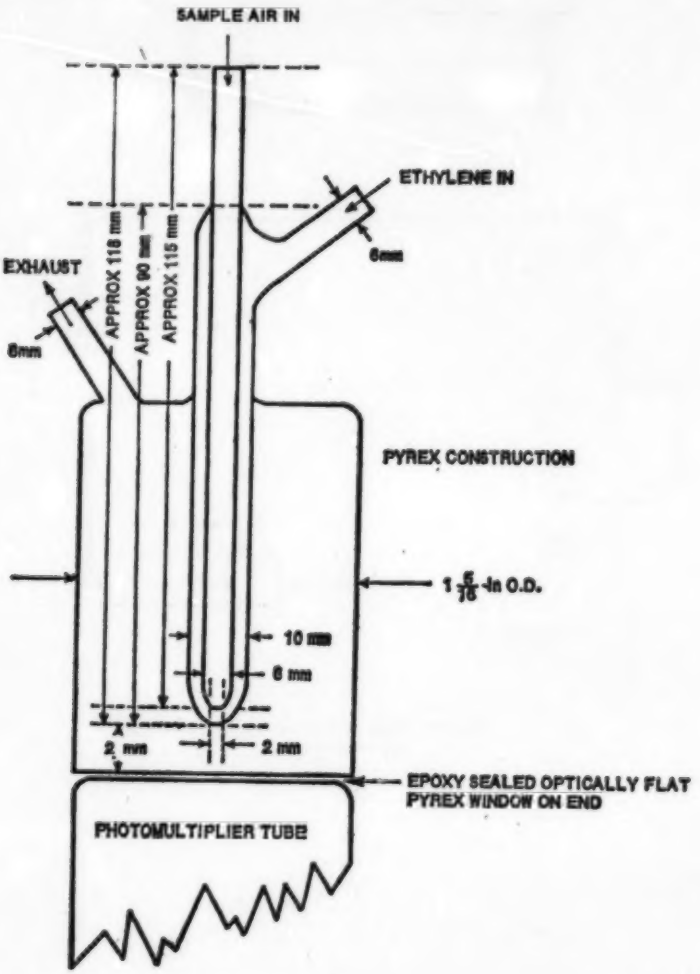

Figure D1. Detector cell.

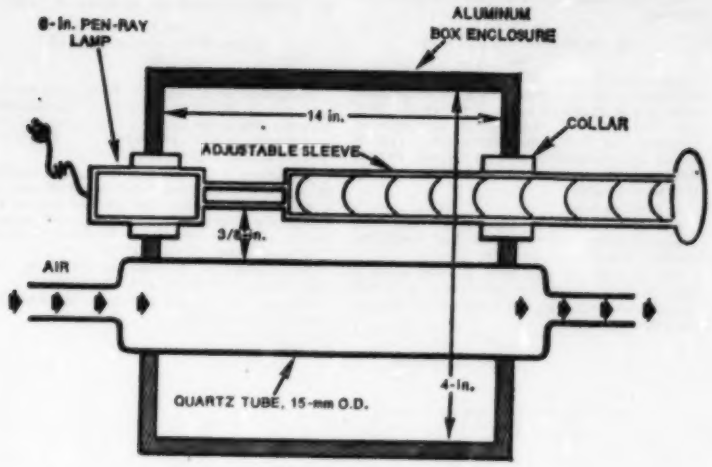

Figure D2. Ozone source.

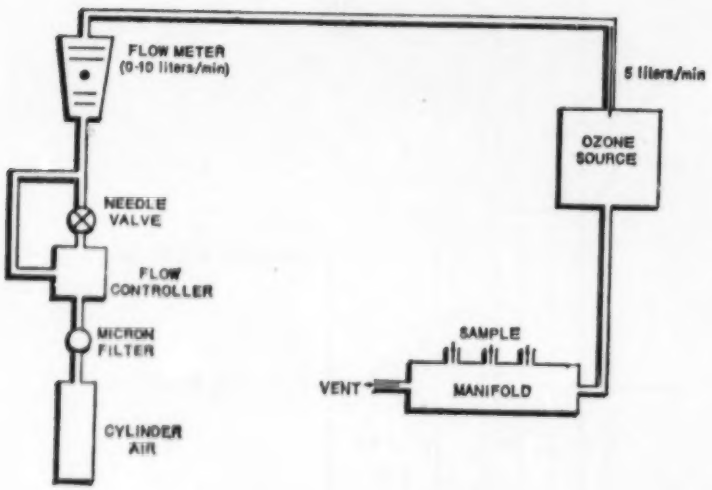

Figure D3. Ozone calibration air supply, source, and manifold system.

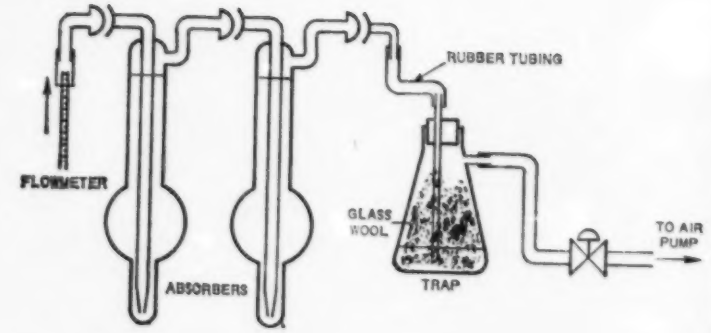

Figure D4. KI sampling train.

ADDENDA

A. Suggested Performance Specifications for Atmospheric Analyzers for Hydrocarbons Corrected for Methane:

Range (minimum)	0–5 p.p.m. THC.
Output (minimum)	0–5 p.p.m. CH_4.
Minimum detectable sensitivity	0–10 mv. full scale.
Zero drift (maximum)	0.1 p.p.m. THC.
Span drift (maximum)	0.1 p.p.m. CH_4.
Precision (minimum)	Not to exceed 1 percent/24 hours.
Operational period (minimum)	Not to exceed 1 percent/24 hours.
Operating temperature range (minimum)	±0 percent.
Operating humidity range (minimum)	3 days.
Linearity (maximum)	5–40° C.
	0–100 percent.
	1 percent of full scale.

B. Suggested Definitions of Performance Specifications:

Range—The minimum and maximum measurement limits.

Output—Electrical signal which is proportional to the measurement; intended for connection to readout or data processing devices. Usually expressed as millivolts or milliamps full scale at a given impedence.

Full Scale—The maximum measuring limit for a given range.

Minimum Detectable Sensitivity—The smallest amount of input concentration that can be detected as the concentration approaches zero.

Accuracy—The degree of agreement between a measured value and the true value; usually expressed at ± percent of full scale.

Lag Time—The time interval from a step change in input concentration at the instrument inlet to the first corresponding change in the instrument output.

Time to 90 Percent Response—The time interval from a step change in the input concentration at the instrument inlet to a reading of 90 percent of the ultimate recorded concentration.

Rise Time (90 percent)—The interval between initial response time and time to 90 percent response after a step decrease in the inlet concentration.

Zero Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is zero; usually expressed as percent full scale.

Span Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation, when the input concentration is a stated upscale value; usually expressed as percent full scale.

Precision—The degree of agreement between repeated measurements of the same concentration. It is expressed as the average deviation of the single results from the mean.

Operational Period—The period of time over which the instrument can be expected to operate unattended within specifications.

Noise—Spontaneous deviations from a mean output not caused by input concentration changes.

Interference—An undesired positive or negative output caused by a substance other than the one being measured.

Interference Equivalent—The portion of indicated input concentration due to the presence of an interferent.

Operating Temperature Range—The range of ambient temperatures over which the instrument will meet all performance specifications.

Operating Humidity Range—The range of ambient relative humidity over which the instrument will meet all performance specifications.

Linearity—The maximum deviation between an actual instrument reading and the reading predicted by a straight line drawn between upper and lower calibration points.

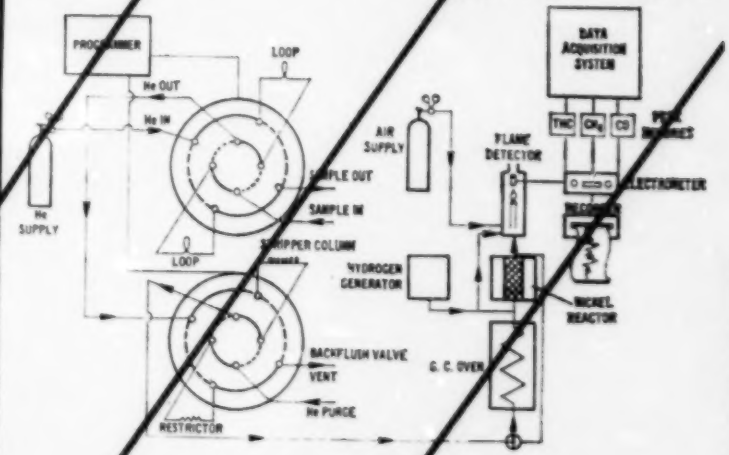

Figure E1. Typical flow diagram.

APPENDIX F—REFERENCE METHOD FOR THE DETERMINATION OF NITROGEN DIOXIDE IN THE ATMOSPHERE (24-HOUR SAMPLING METHOD)

1. *Principle and Applicability.*

1.1 Nitrogen dioxide is collected by bubbling air through a sodium hydroxide solution to form a stable solution of sodium nitrite. The nitrite ion produced during sampling is determined colorimetrically by reacting the exposed absorbing reagent with phosphoric acid, sulfanilamide, and N-1-naphthylethylenediamine dihydrochloride.

1.2 The method is applicable to collection of 24-hour samples in the field and subsequent analysis in the laboratory.

2. *Range and Sensitivity.*

2.1 The range of the analysis is 0.04 to 1.5 μg. NO_2/ml. With 50 ml. absorbing reagent and a sampling rate of 300 ml./min. for 24 hours, the range of the method is 20–740 μg. m.³ (0.01–0.4 p.p.m.) nitrogen dioxide.

2.2 A concentration of 0.04 μg. NO_2/ml. will produce an absorbance of 0.02 using 1-cm. cells.

3. *Interferences.*

3.1 The interference of sulfur dioxide is eliminated by converting it to sulfuric acid with hydrogen peroxide before analysis. (*1*)

4. *Precision, Accuracy, and Stability.*

4.1 The relative standard deviations are 14.4 percent and 8.5 percent at nitrogen dioxide concentrations of 140 μg./m.³ (0.072 p.p.m.) and 200 μg./m.³ (0.108 p.p.m.), respectively, based on an automated analysis of